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APPLICATION NUMBER	PATENT NUMBER	GROUP ART UNIT	FILE WRAPPER LOCATION
10/608,291	7044220	3676	9200

Correspondence Address / Fee Address Change

The following fields have been set to Customer Number 71407 on 10/29/2007

- Correspondence Address
- Maintenance Fee Address

The address of record for Customer Number 71407 is:

ROBERT A. KENT
P.O. BOX 1431
DUNCAN, OK 73536

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail

Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
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or Fax (571) 273-2885

JAN 09 2006

or Fax

INSTRUCTIONS: This form should be used when transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below. Transmittal otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

7590

12/20/2005

Robert A. Kent
Halliburton Energy Services
2600 South 2nd Street
Duncan, OK 73536

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

Tammy Knight	(Depositor's name)
<i>Tammy Knight</i>	(Signature)
1-5-2006	(Date)

01/11/2006 CNGUYEN3 00000016 080300 10608291

01 FC:1501 1400.00 DA
02 FC:1504 300.00 DA

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/608,291	06/27/2003	Philip D. Nguyen	2002-IP-009210U1	8521

TITLE OF INVENTION: COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUBTERRANEAN WELL

APPLN. TYPE	SMALL ENTITY	ISSUE FEE	PUBLICATION FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	NO	\$1400	\$300	\$1700	03/20/2006

EXAMINER	ART UNIT	CLASS-SUBCLASS
SUCHFIELD, GEORGE A	3676	166-280200

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. Use of a Customer Number is required.

2. For printing on the patent front page, list
(1) the names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 Robert A. Kent
2 Baker Botts
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE

Halliburton Energy Services, Inc.

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

Duncan, OK

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are enclosed:

☒ Issue Fee
☒ Publication Fee (No small entity discount permitted)
☐ Advance Order - # of Copies _____

4b. Payment of Fee(s):

☐ A check in the amount of the fee(s) is enclosed.
☐ Payment by credit card. Form PTO-2038 is attached.
☒ The Director is hereby authorized by charge the required fee(s), or credit any overpayment, to Deposit Account Number 08-0300 (enclose an extra copy of this form).

5. Change in Entity Status (from status indicated above)

☐ a. Applicant claims SMALL ENTITY status. See 37 CFR 1.27.☐ b. Applicant is no longer claiming SMALL ENTITY status. See 37 CFR 1.27(g)(2).

The Director of the USPTO is requested to apply the Issue Fee and Publication Fee (if any) or to re-apply any previously paid issue fee to the application identified above.
NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature

Robert A. Kent

Date

1-5-2006

Typed or printed name

Robert A. Kent

Registration No. 28,626

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

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NOTICE OF ALLOWANCE AND FEE(S) DUE

7590 12/20/2005

Robert A. Kent
Halliburton Energy Services
2600 South 2nd Street
Duncan, OK 73536

EXAMINER

SUCHFIELD, GEORGE A

ART UNIT

PAPER NUMBER

3676

DATE MAILED: 12/20/2005

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/608,291	06/27/2003	Philip D. Nguyen	2002-IP-009210U1	8521

TITLE OF INVENTION: COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUBTERRANEAN WELL

APPLN. TYPE	SMALL ENTITY	ISSUE FEE	PUBLICATION FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	NO	\$1400	\$300	\$1700	03/20/2006

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. **PROSECUTION ON THE MERITS IS CLOSED.** THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN **THREE MONTHS** FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. **THIS STATUTORY PERIOD CANNOT BE EXTENDED.** SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE REFLECTS A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE APPLIED IN THIS APPLICATION. THE PTOL-85B (OR AN EQUIVALENT) MUST BE RETURNED WITHIN THIS PERIOD EVEN IF NO FEE IS DUE OR THE APPLICATION WILL BE REGARDED AS ABANDONED.

HOW TO REPLY TO THIS NOTICE:

I. Review the SMALL ENTITY status shown above.

If the SMALL ENTITY is shown as YES, verify your current SMALL ENTITY status:

A. If the status is the same, pay the TOTAL FEE(S) DUE shown above.

B. If the status above is to be removed, check box 5b on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and twice the amount of the ISSUE FEE shown above, or

If the SMALL ENTITY is shown as NO:

A. Pay TOTAL FEE(S) DUE shown above, or

B. If applicant claimed SMALL ENTITY status before, or is now claiming SMALL ENTITY status, check box 5a on Part B - Fee(s) Transmittal and pay the PUBLICATION FEE (if required) and 1/2 the ISSUE FEE shown above.

II. PART B - FEE(S) TRANSMITTAL should be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). Even if the fee(s) have already been paid, Part B - Fee(s) Transmittal should be completed and returned. If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

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(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
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1	_____
2	_____
3	_____

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(A) NAME OF ASSIGNEE

(B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☐ Corporation or other private group entity ☐ Government

4a. The following fee(s) are enclosed:

- ☐ Issue Fee
- ☐ Publication Fee (No small entity discount permitted)
- ☐ Advance Order - # of Copies _____

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- ☐ Payment by credit card. Form PTO-2038 is attached.
- ☐ The Director is hereby authorized by charge the required fee(s), or credit any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

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- ☐ a. Applicant claims SMALL ENTITY status. See 37 CFR 1.27.
- ☐ b. Applicant is no longer claiming SMALL ENTITY status. See 37 CFR 1.27(g)(2).

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Authorized Signature _____

Date _____

Typed or printed name _____

Registration No. _____

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/608,291	06/27/2003	Philip D. Nguyen	2002-IP-009210U1	8521
7590 12/20/2005			EXAMINER	
Robert A. Kent Halliburton Energy Services 2600 South 2nd Street Duncan, OK 73536			SUCHFIELD, GEORGE A	
			ART UNIT	PAPER NUMBER
			3676	

DATE MAILED: 12/20/2005

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b) (application filed on or after May 29, 2000)

The Patent Term Adjustment to date is 149 day(s). If the issue fee is paid on the date that is three months after the mailing date of this notice and the patent issues on the Tuesday before the date that is 28 weeks (six and a half months) after the mailing date of this notice, the Patent Term Adjustment will be 149 day(s).

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (<http://pair.uspto.gov>).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571) 272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at (703) 305-8283.

Notice of Allowability

Application No.

10/608,291

Examiner

George Suchfield

Applicant(s)

NGUYEN ET AL.

Art Unit

3676

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to 10/11/05.
2. ☒ The allowed claim(s) is/are 1-38 and 73-107.
3. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some* c) ☐ None of the:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

* Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

4. ☐ A SUBSTITUTE OATH OR DECLARATION must be submitted. Note the attached EXAMINER'S AMENDMENT or NOTICE OF INFORMAL PATENT APPLICATION (PTO-152) which gives reason(s) why the oath or declaration is deficient.
5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
- (a) ☐ including changes required by the Notice of Draftsperson's Patent Drawing Review (PTO-948) attached
- 1) ☐ hereto or 2) ☐ to Paper No./Mail Date _____.
- (b) ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.
- Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3. ☒ Information Disclosure Statements (PTO-1449 or PTO/SB/08),
Paper No./Mail Date 6/17/05; 7/21/05; 8/19/05; 10/11/05
4. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
5. ☐ Notice of Informal Patent Application (PTO-152)
6. ☒ Interview Summary (PTO-413),
Paper No./Mail Date 12/8/05
7. ☒ Examiner's Amendment/Comment
8. ☐ Examiner's Statement of Reasons for Allowance
9. ☐ Other _____.

George Suchfield
Primary Examiner
Art Unit: 3676

1. An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in a telephone interview with Robert A. Kent on December 8, 2005.

The application has been amended as follows:


In claim 73, line 4, after "composite material", the following recitation has been inserted:
-- that comprises one or more poly(orthoesters) -- .

Any inquiry concerning this communication or earlier communications from the examiner should be directed to George Suchfield whose telephone number is 571-272-7036. The examiner can normally be reached on M-F (6:30 - 3:00).

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brian Glessner can be reached on 571-272-6843. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Art Unit: 3676

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).


George Suchfield
Primary Examiner
Art Unit 3676

Gs
December 9, 2005

Examiner-Initiated Interview Summary	Application No.	Applicant(s)	
	10/608,291	NGUYEN ET AL.	
	Examiner	Art Unit	
	George Suchfield	3676	

All Participants:

(1) George Suchfield.

(2) Robert A. Kent.

Date of Interview: 8 December 2005

Type of Interview:
☒ Telephonic
☐ Video Conference
☐ Personal (Copy given to: ☐ Applicant ☐ Applicant's representative)

Exhibit Shown or Demonstrated: ☐ Yes ☒ No
 If Yes, provide a brief description: _____

Part I.

Rejection(s) discussed:
35 USC 102

Claims discussed:
1 and new claim 73

Prior art documents discussed:
Cooke, Jr. (2003/0060374)

Part II.

SUBSTANCE OF INTERVIEW DESCRIBING THE GENERAL NATURE OF WHAT WAS DISCUSSED:
See Continuation Sheet

Part III.

☐ It is not necessary for applicant to provide a separate record of the substance of the interview, since the interview directly resulted in the allowance of the application. The examiner will provide a written summary of the substance of the interview in the Notice of Allowability.

☒ It is not necessary for applicant to provide a separate record of the substance of the interview, since the interview did not result in resolution of all issues. A brief summary by the examiner appears in Part II above.

Status of Application: pending

(3) _____

(4) _____

Time: Eastern Standard, p.m.

(Examiner/SPE Signature)

(Applicant/Applicant's Representative Signature – if appropriate)

Continuation of Substance of Interview including description of the general nature of what was discussed: It was indicated by the examiner that new claim 73 appeared to read on the reference to Cooke, Jr.'374, applied in the previous Office action, insofar as the degradable pellet of Cooke, Jr. appeared to comprise or read on the recited "degradable composite material" (note, e.g., Para [0030] on page 5). The examiner further indicated the amendment to claim 1 wherein the degradable material is now limited to "one or more poly(orthoesters)" was still under consideration, whereupon the attorney emphasized the arguments/traversal set forth in the REMARKS of the amendment, most specifically, that the Anton Skrabal & Otto Ringer reference, with accompanying translation, noted on page 13, provided evidence/explanation that the/a "poly(orthoester)" possessed the chemical structure and properties/reactiveness of an ether, rather than an ester, and thus patentably distinguishes over the reference to Cooke, Jr., and other cited/applied references. No agreement was reached, however, applicant's attorney gave the examiner authorization to amend new claim 73 to include the same claim 1 limitation: "that comprises one or more poly(otheesters)", in the event the examiner did determine claim 1 to be allowable..

PTO-1449 JUN 17 2005
 Information Disclosure Citation
 in an Application

Application No.
 10/608,291

Applicant(s):
 PHILIP NGUYEN ET AL.

Docket Number
 2002-IP-009210U1

Group Art Unit
 3672

Filing Date
 June 27, 2003

U.S. PATENT DOCUMENTS

	DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE
1.	3,173,484	03/16/65	Hultt, et al.	166	280.1	09/02/58
2.	3,195,635	07/20/65	Fast	166	280.1	05/23/63
3.	3,302,719	02/07/67	Fischer	166	280.2	01/25/65
4.	3,364,995	01/23/68	Atkins, et al.	166	280.1	02/14/66
5.	3,366,178	01/30/68	Malone, et al.	166	280.1	09/10/65
6.	3,455,390	07/15/69	Gallus	166	295	12/03/65
7.	3,968,840	07/13/76	Tate	166	280.1	05/25/73
8.	3,998,744	12/21/76	Arnold, et al.	507	269	04/16/75
9.	4,068,718	01/17/78	Cooke, Jr., et al.	166	280.2	10/26/76

FOREIGN PATENT DOCUMENTS

	DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION YES NO
1.	WO 2004/007905	01/22/04	PCT	E21B	43/27	X
2.	WO 2000/57022	09/28/00	PCT	E21B	37/06	X
3.	WO 2001/02698	01/11/01	PCT	E21B	43/27	X

NON-PATENT DOCUMENTS

	DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE
1.	Y. CHIANG ET AL.: "HYDROLYSIS OF ORTHO ESTERS: FURTHER INVESTIGATION OF THE FACTORS WHICH CONTROL THE RATE-DETERMINING STEP," ENGINEERING INFORMATION INC., NY, NY, VOL. 105, No. 23 (XP-002322842)	11/16/83
2.	M. AHMAD, ET AL.: "ORTHO ESTER HYDROLYSIS: DIRECT EVIDENCE FOR A THREE-STAGE REACTION MECHANISM," ENGINEERING INFORMATION INC., NY, NY, VOL. 101, No. 10 (XP-002322843)	05/09/79

EXAMINER
 George Suchfield

DATE CONSIDERED
 12/19/05

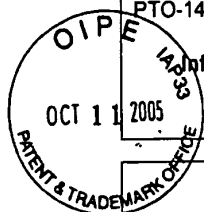
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.

PTO-1449	Application No. 10/608,291	Applicant(s): Philip D. Nguyen, et al.	
	Docket Number 2002-IP-009210U1	Group Art Unit 3672 3676	Filing Date: 06/27/2003

U.S. PATENT DOCUMENTS						
	DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE
CS	5,607,905	03/04/97	Dobson, Jr. et al.	507	211	03/15/94
	6,394,185 B1	05/28/02	Constien	166	296	07/27/00
	6,761,218 B2	07/13/04	Nguyen et al.	166	278	04/01/02
CS	US 2002/0125012 A1	09/12/02	Dawson et al.	166	300	01/08/02

NON-PATENT DOCUMENTS		DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE
CS		SKRABAL ET AL., <i>THE HYDROLYSIS RATE OF ORTHOFORMIC ACID ETHYL ETHER</i> , CHEMICAL INSTITUTE OF THE UNIVERSITY OF GRAZ, PAGES 1-38	01/13/21
		Heller, et al., <i>Poly(ortho esters) – From Concept To Reality</i> , Biomacromolecules, Vol. 5, No. 5, 2004 (pp. 1625-1632)	05/09/79
		Schwach-Abdellaoui, et al., <i>Hydrolysis and Erosion Studies of Autocatalyzed Poly(ortho esters) Containing Lactoyl-Lactyl Acid Dimers</i> , American Chemical Society, Vol. 32, No. 2, 1999 (pp. 301-307)	
		Ng, et al., <i>Synthesis and Erosion Studies of Self-Catalyzed Poly(ortho ester)s</i> , American Chemical Society, Vol. 30, No. 4, 1997 (pp. 770-772)	
		Ng, et al., <i>Development Of A Poly(ortho ester) prototype With A Latent Acid In The Polymer Backbone For 5-fluorouracil Delivery</i> , Journal of Controlled Release 65 (2000), (pp. 367-374)	
		Rothen-Weinhold, et al., <i>Release of BSA from poly(ortho ester) extruded thin strands</i> , Journal of Controlled Release 71, 2001, (pp. 31-37)	
		Heller, et al., <i>Poly(ortho esters) – their development and some recent applications</i> , European Journal of Pharmaceutics and Biopharmaceutics, 50, 2000, (pp. 121-128)	
		Heller, et al., <i>Poly(ortho esters); synthesis, characterization, properties and uses</i> , Advanced Drug Delivery Reviews, 54, 2002, (pp. 1015-1039)	
		Heller, et al., <i>Poly(ortho esters) For The Pulsed And Continuous Delivery of Peptides And Proteins</i> , Controlled Release and Biomedical Polymers Department, SRI International, (pp. 39-46)	
		Zignani, et al., <i>Subconjunctival biocompatibility of a viscous bioerodable poly(ortho ester)</i> , J. Biomed Mater Res, 39, 1998, pp. 277-285	
		Toncheva, et al., <i>Use of Block Copolymers of Poly(Ortho Esters) and Poly (Ethylene Glycol)</i> , Journal of Drug Targeting, 2003, Vol. 11(6), pp. 345-353	
		Schwach-Abdellaoui, et al., <i>Control of Molecular Weight For Auto-Catalyzed Poly(ortho ester) Obtained by Polycondensation Reaction</i> , International Journal of Polymer Anal. Charact., 7: 145-161, 2002, pp. 145-161	
CS		Heller, et al., <i>Release of Norethindrone from Poly(Ortho Esters)</i> , Polymer Engineering and Science, Mid-August, 1981, Vol. 21, No. 11 (pp. 727-731)	

EXAMINER George Suchfield	DATE CONSIDERED 12/9/05
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.	



PTO-1449	Application No. 10/608,291	Applicant(s): Philip D. Nguyen, et al.	
Information Disclosure Citation In an Application	Docket Number 2002-IP-009210U1	Group Art Unit 36726	Filing Date 06/27/2003


U.S. PATENT DOCUMENTS

	DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE

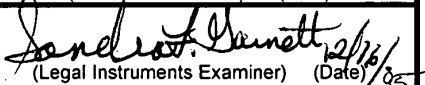
NON-PATENT DOCUMENTS

	DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE
69	Cordes, et al., <i>Mechanism and Catalysis for Hydrolysis of Acetals, Ketals, and Other Esters</i> , Department of Chemistry, Indiana University, Bloomington, Indiana, Chemical Reviews, 1974, Vol. 74, No. 5, pp. 581-603	—
69	TODD, ET AL., A CHEMICAL "TRIGGER" USEFUL FOR OILFIELD APPLICATIONS, SOCIETY OF PETROLEUM ENGINEERS, INC., SPE 92709	02/04/05

EXAMINER George Suchfield	DATE CONSIDERED 12/9/05
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.	

Issue Classification 	Application/Control No.	Applicant(s)/Patent under Reexamination	
	10/608,291	NGUYEN ET AL.	
	Examiner	Art Unit	
	George Suchfield	3676	

ISSUE CLASSIFICATION											
ORIGINAL					CROSS REFERENCE(S)						
CLASS		SUBCLASS		CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)						
166		280.2		166	280.1	281	300				
INTERNATIONAL CLASSIFICATION				507	209	211	219	220	260	273	906
E	2	1	B	43/267	507	924					
E	2	1	B	33/138	523	131					
				/							
				/							
				/							

(Assistant Examiner) (Date)		George Suchfield George Suchfield 12/9/05 (Primary Examiner) (Date)		Total Claims Allowed: 73	
 (Legal Instruments Examiner) (Date) 12/16/05				O.G. Print Claim(s) 1	
				O.G. Print Fig. —	

<input checked="" type="checkbox"/> Claims renumbered in the same order as presented by applicant												<input type="checkbox"/> CPA		<input type="checkbox"/> T.D.		<input type="checkbox"/> R.1.47	
Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
	1		31		61		91		121		151		181				
	2		32		62		92		122		152		182				
	3		33		63		93		123		153		183				
	4		34		64		94		124		154		184				
	5		35		65		95		125		155		185				
	6		36		66		96		126		156		186				
	7		37		67		97		127		157		187				
	8		38		68		98		128		158		188				
	9		39		69		99		129		159		189				
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	11		41		71		101		131		161		191				
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	20		50		80		110		140		170		200				
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	22		52		82		112		142		172		202				
	23		53		83		113		143		173		203				
	24		54		84		114		144		174		204				
	25		55		85		115		145		175		205				
	26		56		86		116		146		176		206				
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	29		59		89		119		149		179		209				
	30		60		90		120		150		180		210				



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Bib Data Sheet

CONFIRMATION NO. 8521

SERIAL NUMBER 10/608,291	FILING DATE 06/27/2003 RULE	CLASS 166	GROUP ART UNIT 3676	ATTORNEY DOCKET NO. 2002-IP-009210U1
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APPLICANTS

Philip D. Nguyen, Duncan, OK;
 Bradley L. Todd, Duncan, OK;
 Trinidad Munoz JR., Duncan, OK;

** CONTINUING DATA ***** GS

** FOREIGN APPLICATIONS *****

IF REQUIRED, FOREIGN FILING LICENSE GRANTED
 ** 09/23/2003

Foreign Priority claimed <input type="checkbox"/> yes <input checked="" type="checkbox"/> no	STATE OR COUNTRY OK	SHEETS DRAWING 0	TOTAL CLAIMS 68	INDEPENDENT CLAIMS 4
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35 USC 119 (a-d) conditions met
☐ yes ☒ no ☐ Met after


Verified and Acknowledged
 Allowance
Gloria Luckfield
 Examiner's Signature Initials

ADDRESS
 Robert A. Kent
 Halliburton Energy Services
 2600 South 2nd Street
 Duncan, OK
 73536

TITLE
 Compositions and methods for improving proppant pack permeability and fracture conductivity in a subterranean well

FILING FEE RECEIVED 2234	FEES: Authority has been given in Paper No. _____ to charge/credit DEPOSIT ACCOUNT No. _____ for following:	<input type="checkbox"/> All Fees <input type="checkbox"/> 1.16 Fees (Filing) <input type="checkbox"/> 1.17 Fees (Processing Ext. of time) <input type="checkbox"/> 1.18 Fees (Issue)
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	<input type="checkbox"/> Other _____
	<input type="checkbox"/> Credit

Search Notes 		Application/Control No. 10/608,291		Applicant(s)/Patent under Reexamination NGUYEN ET AL.	
		Examiner George Suchfield		Art Unit 3676	

SEARCHED			
Class	Subclass	Date	Examiner
166	276, 278, 280.1, 280.2, 281		
	295, 300		
	308.1		
	308.2		
507	209, 211		
	219, 220		
	260, 273		
	906, 924		
523	130, 131	12/9/2005	G.S.

INTERFERENCE SEARCHED			
Class	Subclass	Date	Examiner
EAST - PGPubs (see printout)		12/9/2005	G.S.

SEARCH NOTES (INCLUDING SEARCH STRATEGY)		
	DATE	EXMR



Practitioner's Docket No. 2002-IP-009210U1

PATENT

ifw

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Philip D. Nguyen, et al.

Group No. 3672

Application No.: 10/608,291 Examiner: unknown

Filed: 6/27/2003

For: COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK
PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUBTERREAN WELL

Mail Stop Amendment

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

STATEMENT FOR INFORMATION DISCLOSURE UNDER
37 C.F.R. § 1.97(e)

NOTE: A statement must state either: "(1) that each item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement, or (2) that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and to the knowledge of the person signing the statement after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the information disclosure statement." 37 C.F.R. § 1.97(e).

Under the first statement under § 1.97(e), it does not matter whether any individual with a duty of disclosure actually knew about any of the information cited before receiving the search report. The date on the communication by the foreign patent office begins the 3-month period in the same manner as the mailing of an Office action starts a 3-month shortened statutory period for reply. See § 609B(5), M.P.E.P., 8th Edition.

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*

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Express Mail certification is optional.)

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☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 12.5.05

Signature

Chasidy Smith

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [8-8]—page 1 of 5)

NOTE: "Section 1.97(e) makes it clear that a certification could contain either of two statements. One statement is that each item of information in an information disclosure statement was cited in a search report from a patent office outside the U.S. not more than three months prior to the filing date of the statement. Under this certification, it would not matter whether any individual with a duty actually knew about any of the information cited before receiving the search report. In the alternative, the certification could state that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to the knowledge of the person signing the certification after making reasonable inquiry, was known to any individual having a duty to disclose more than three months prior to the filing of the statement." Notice of January 9, 1992, 1135 O.G. 13-25, at 13. (emphasis added). Thus: "If an item of information is submitted within three months of being cited in a communication from a foreign patent office in a counterpart foreign application, the certification can be properly made regardless of any individual's previous knowledge of the information." *Id.*, 1135 O.G. at 19. See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "The date on the communication by the foreign patent office begins the 3-month period in the same manner as the mailing of an Office action starts a 3-month shortened statutory period for reply. If the communication contains two dates, the mailing date of the communication is the one which begins the 3-month period. The date which begins the 3-month period is not the date the communication was received by a foreign associate or the date it was received by a U.S. registered practitioner. Likewise, the statement will be considered to have been filed on the date the statement was received in the Office, or on an earlier date of mailing or transmission if accompanied by a properly executed certificate of mailing or facsimile transmission under 37 CFR 1.8, or if it is in compliance with the provisions for "Express Mail" delivery under 37 C.F.R. 1.10." See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "The certification can be based on present, good faith knowledge about when information became known without a search of files being made." Thus, for example, the certification of § 1.97(e) does not preclude the use of the certification in an application by corporations whose practitioners have over the years reviewed thousands of patents and technical publications, even though they are unaware of the relevance of any one thereof to the application. Notice of January 9, 1992, 1135 O.G. 13-15, at 19.

See § 609B(5), M.P.E.P., 8th Edition:

"If an information disclosure statement includes a copy of a dated communication from a foreign patent office which clearly shows that the statement is being submitted within 3 months of the date on the communication, the copy will be accepted as the required communication. It will be assumed, in the absence of evidence to the contrary, that the communication was for a counterpart foreign application.

"In the alternative, a statement can be made if no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to the knowledge of the person signing the statement after making reasonable inquiry, neither was it known to any individual having a duty to disclose more than 3 months prior to the filing of the statement."

NOTE: A copy of the foreign search report need not be submitted with the certification. Notice of April 20, 1992 (1138 O.G. 37-41, 40).

NOTE: "The phrase 'after making reasonable inquiry' makes it clear that the individual making the statement has a duty to make reasonable inquiry regarding the facts that are being certified. The statement can be made by a registered practitioner who represents a foreign client and who relies on statements made by the foreign client as to the date the information first became known. A registered practitioner who receives information from a client without being informed whether the information was known for more than three months, however, cannot make the statement without making reasonable inquiry. For example, if an inventor gave a publication to the attorney prosecuting an application with the intent that it be cited to the Office, the attorney should inquire as to when that inventor became aware of the publication and should not submit a statement under 37 C.F.R. 1.97(e)(2) to the Office until a satisfactory response is received. The statement can be based on present, good faith knowledge about when information became known without a search of files being made." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "Although it is recognized that an individual actually becomes aware of the information in the communication from a foreign patent office sometime after it was mailed, the mailing date of such a communication, if it occurs prior to a first awareness of the same information, would determine the date for filing of an information disclosure statement without a fee" in a certification procedure under § 1.97(e). Notice of January 9, 1992, 1135 O.G. 13-25, at 19 (emphasis added).

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [6-8]—page 2 of 5)

NOTE: *The mere absence of an item of information from a foreign patent office communication is not intended to represent an opportunity to delay the submission of a item known more than three months prior to the filing of an information disclosure statement to an individual having the duty of disclosure under § 1.56. 62 Fed. Reg. 53,131, 53,150 (Oct. 10, 1997).*

NOTE: *The IDS is considered filed as of the date it is received in the PTO, or on an earlier date of mailing or transmission if done so with a properly executed certificate of mailing or facsimile transmission under 37 C.F.R. § 1.8, or if it is in compliance with the provisions for "Express Mail" delivery under 37 C.F.R. § 1.10. See § 609B(5), M.P.E.P., 8th Edition.*

NOTE: *"The certification under § 1.97(e) should be made by a person who has knowledge of the facts being certified. The certification can be made by a practitioner who represents a foreign client and who relies on statements made by the foreign client as to the date the information first became known. A practitioner who receives information from a client without being informed whether the information was known for more than three months, however, cannot make the certification without making reasonable inquiry." Notice of January 9, 1992, 1135 O.G. 13-25 at 19.*

NOTE: *"The term counterpart foreign patent application means that a claim for priority has been made in either the U.S. application or a foreign application based on the other, or that the disclosures of the U.S. and foreign patent applications are substantively identical (e.g., an application filed in the European Patent Office claiming the same U.K. priority as claimed in the U.S. application)." Notice of April 20, 1992 (1138 O.G. 37-41, 39). See § 609B(5), M.P.E.P., 8th Edition.*

NOTE: *"Individuals other than the attorney, agent or inventor may comply with this section by disclosing information to the attorney, agent or inventor." 37 C.F.R. § 1.56(d) and*

"Individuals associated with the filing or prosecution of a patent application within the meaning of this section are:

(1) each inventor named in the application;

(2) each attorney or agent who prepares or prosecutes the application; and

(3) every other person who is substantively involved in the preparation or prosecution of the application and who is associated with the inventor, with the assignee or with anyone to whom there is an obligation to assign the application." 37 C.F.R. § 1.56(c).

IDENTIFICATION OF INFORMATION DISCLOSURE STATEMENT FOR WHICH THIS STATEMENT IS BEING MADE

1. This statement is being made for the Information Disclosure Statement

☒ accompanying this statement.

☐ filed _____ (date)

STATEMENT

NOTE: *A statement under 37 C.F.R. § 1.97(e) need not be in the form of an oath or a declaration under 37 C.F.R. § 1.68. A statement under 37 C.F.R. § 1.97(e) by a registered practitioner or any other individual that the statement was filed within the 3-month period of either the first citation by a foreign patent office or first discovery of the information will be accepted as dispositive of compliance with this provision in the absence of evidence to the contrary. § 609B(5), M.P.E.P., 8th Edition.*

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [6-8]—page 3 of 5)

2. I, the person(s) signing below state:

- ☐ that each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. 37 C.F.R. § 1.97(e)(1).

NOTE: *The three month period starts from the mailing date of the foreign patent office communication. Notice of January 9, 1992, 1135 O.G. 13-25 at 19. The mailing date is the "date on the communication by the foreign patent office." Notice of April 20, 1992 (1138 O.G. 37-41, 39).*

OR

- ☒ that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to my knowledge, after making reasonable inquiry, no item of information contained in this information disclosure statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the information disclosure statement. 37 C.F.R. § 1.97(e)(2).

NOTE: *"The time at which information 'was known to any individual designated in 37 C.F.R. 1.56(c)' is the time when the information was discovered in association with the application even if awareness of the materiality came later." Notice of April 20, 1992 (1138 O.G. 37-41, 40). Section 609B(5), M.P.E.P., 8th Edition.*

IDENTIFICATION OF PERSON(S) MAKING THIS STATEMENT

3. The person making this statement is

(check each applicable item)

- (a) ☐ the inventor(s) who signs below

SIGNATURE OF INVENTOR

(type name of inventor who is signing)

- (b) ☐ a person who is substantively involved in the preparation or prosecution of the application, and who is associated with the inventor, with the assignee, or with anyone to whom there is an obligation to assign the application (37 C.F.R. § 1.56(c)) and who signs below.

SIGNATURE OF PERSON MAKING STATEMENT

(type name of person who is signing)

Address of person who is signing

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [6-8]—page 4 of 5)

(c) ☒ the practitioner who signs below on the basis of the information:

(check each applicable item)

- ☐ supplied by the inventor(s).
- ☐ supplied by an individual designated in § 1.56(c).
- ☒ in the practitioner's file.

Reg. No.: 28,626

Tel. No. (580)-251-3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

PO BOX 1431

P.O. Address

DUNCAN OK 73536-0440

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [6-8]—page 5 of 5)



2002-IP-009210U1

Practitioner's Docket No. _____

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Philip D Nguyen, et al.

Application No: 10/608,291

Group No.: 3672

Filed: 6/27/2003

Examiner: unknown

For: COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK
PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUBTERREAN WELL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
BEFORE MAILING DATE OF EITHER A FINAL ACTION
OR NOTICE OF ALLOWANCE (37 C.F.R. § 1.97(c))**

NOTE: 37 C.F.R. 1.97: "(c) An information disclosure statement shall be considered by the Office if filed after the period specified in paragraph (b) of this section, provided that the information disclosure statement is filed before the mailing date of any of a final action under § 1.113, a notice of allowance under § 1.311, or an action that otherwise closes prosecution in the application, and it is accompanied by one of:

- (1) The statement specified in paragraph (a) of this section; or
- (2) The fee set forth in § 1.17(p)."

NOTE: "If a final action or notice of allowance is mailed in an application and later withdrawn, the application will be considered as not having had a final action or notice of allowance mailed for purposes of considering an information disclosure statement." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10 *

☒ with sufficient postage as first class mail.

☐ as "Express Mail Post Office to Addressee"

Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 12/5/05

Signature

Tammy Knight

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(c)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [8-4]—page 1 of 3)

BEST AVAILABLE COPY

NOTE: 37 C.F.R. § 1.704(d): "A paper containing only an information disclosure statement in compliance with §§ 1.97 and 1.98 will not be considered a failure to engage in reasonable efforts to conclude prosecution (processing or examination) of the application under paragraphs (c)(6), (c)(8), (c)(9), or (c)(10) of this section if it is accompanied by a statement that each item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart application and that this communication was not received by any individual designated in § 1.56(c) more than thirty days prior to the filing of the information disclosure statement. This thirty-day period is not extendable."

NOTE: "If information submitted during the period set forth in 37 C.F.R. 1.97(c) with a certification is used in a new ground of rejection on unamended claims, the next Office action will not be made final since in this situation it is clear that applicant has submitted the information to the office promptly after it has become known and the information is being submitted prior to a final determination on patentability by the Office. However, the information submitted with a certification can be used in a new ground of rejection and the next Office action made final, if the new ground of rejection was necessitated by amendment of the application by applicant. Where the information is submitted during this period with a fee, the examiner may use the information submitted, e.g., printed publication or evidence of public use, and make the next Office action final whether or not the claims have been amended, provided that no other new ground of rejection which was not necessitated by amendment to the claims is introduced by the examiner. See MPEP 708.07(a). If a new ground of rejection is introduced that is neither necessitated by an amendment to the claims nor based on the information submitted with the fee set forth in 37 C.F.R. § 1.17(p), the Office action shall not be made final." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

WARNING: "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1992 (1141 O.G. 63). But see § 103(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(d) and in a request for continued examination (RCE) under § 1.114.

WARNING: No extension of time can be had under 37 C.F.R. 1.136 (a) or (b) for filing an IDS. 37 C.F.R. 1.97(f).

TIME OF TRANSMITTAL OF ACCOMPANYING INFORMATION DISCLOSURE STATEMENT

1. The information disclosure statement transmitted herewith is being filed *after* three months of the filing date of this national application or the date of entry of the national stage as set forth in § 1.491 in an international application or after the mailing date of the first Office action on the merits, whichever event occurred last but *before* the mailing date of either:

- (1) a final action under § 1.113 or
 - (2) a notice of allowance under § 1.311,
- whichever occurs first.

STATEMENT ON FEE

2. Accompanying this transmittal is

(check either A or B below)

- A. ☒ a statement as specified in 37 C.F.R. § 1.97(e).

OR

- B. ☐ the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(c). (\$180.00).

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance. [B-4]—page 2 of 3)

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FEE PAYMENT

(complete this item, if applicable)

3. Applicant elects the option to pay the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(c) (\$180.00).

Fee due \$ _____

METHOD OF PAYMENT OF FEE


4.

- ☐ Attached is a ☐ check ☐ money order in the amount of \$ _____
- ☐ Authorization is hereby made to charge the amount of \$ _____
- ☒ to Deposit Account No. 08-0300
- ☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

WARNING: Credit card information should not be included on this form as it may become public.

- ☒ Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

A duplicate of this paper is attached.



SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

P.O. Box 1431

P.O. Address

Duncan, OK 73536-0440

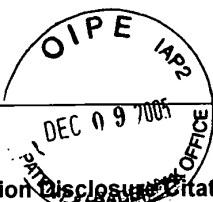
Reg. No. 28,626

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Customer No.:

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [8-4]—page 3 of 3)

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PTO-1449 Information Disclosure Citation in an Application		Application No. 10/608,291		Applicant(s): PHILIP D. NGUYEN, ET AL.	
Docket Number 2003-IP-009210U1		Group Art Unit 3672		Filing Date 06/27/2003	

U.S. PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE
1.		6,702,023 B1	03/09/04	Harris, et al.	166	307	03/07/00
2.		6,817,414 B2	11/16/04	Lee	166	278	09/20/02
3.		2004/0094300 A1	05/20/04	Sullivan, et al.	166	308.1	11/14/03
4.		2005/0103496 A1	05/19/05	Todd, et al.	166	278	11/18/03
5.		2005/0252659 A1	11/17/05	Sullivan, et al.	166	280.1	06/22/05

FOREIGN PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION
							YES NO

NON-PATENT DOCUMENTS	
DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE

EXAMINER	DATE CONSIDERED
----------	-----------------

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	0	(poly\$1ortho\$1ester\$1 WITH (fracture\$1 or fracturing) WITH increasing NEAR3 conductivity WITH subterranean WITH degradable WITH proppant\$1).clm.	US-PGPUB	OR	OFF	2005/12/09 09:46

-GS

PATENT APPLICATION FEE DETERMINATION RECORD
Effective January 1, 2003

Application or Docket Number

10.60.58291

CLAIMS AS FILED - PART I

	(Column 1)	(Column 2)
TOTAL CLAIMS	68	
FOR	NUMBER FILED	NUMBER EXTRA
TOTAL CHARGEABLE CLAIMS	68 minus 20 =	48
INDEPENDENT CLAIMS	1 minus 3 =	
MULTIPLE DEPENDENT CLAIM PRESENT		<input type="checkbox"/>

If the difference in column 1 is less than zero, enter "0" in column 2.

CLAIMS AS AMENDED - PART II

	(Column 1)	(Column 2)	(Column 3)	(Column 4)
AMENDMENT A	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	
Total	21	Minus	28	
Independent	3	Minus	3	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				<input type="checkbox"/>

20 36 34

6.25.04

	(Column 1)	(Column 2)	(Column 3)	(Column 4)
AMENDMENT B	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	
Total		Minus		
Independent		Minus		
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				<input type="checkbox"/>

	(Column 1)	(Column 2)	(Column 3)	(Column 4)
AMENDMENT C	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	
Total	13	Minus	68	5
Independent	4	Minus	3	1
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM				<input type="checkbox"/>

7. If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
 8. If the "Highest Number Previously Paid For" in THIS SPACE is less than 20, enter "20".
 9. If the "Highest Number Previously Paid For" in THIS SPACE is less than 3, enter "3".
 The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

SMALL ENTITY TYPE <input type="checkbox"/>		OTHER THAN SMALL ENTITY <input type="checkbox"/>	
RATE	FEE	RATE	FEE
BASIC FEE	375.00	BASIC FEE	750.00
X3.9 =		X3.9 =	364
X4 =		X4 =	84
+140 =		+140 =	
TOTAL		TOTAL	16.95

SMALL ENTITY TYPE <input type="checkbox"/>		OTHER THAN SMALL ENTITY <input type="checkbox"/>	
RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
X3.9 =		X3.9 =	
X42 =		X42 =	
+140 =		+140 =	
TOTAL ADDIT. FEE		TOTAL ADDIT. FEE	

SMALL ENTITY TYPE <input type="checkbox"/>		OTHER THAN SMALL ENTITY <input type="checkbox"/>	
RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
X3.9 =		X3.9 =	
X42 =		X42 =	
+140 =		+140 =	
TOTAL ADDIT. FEE		TOTAL ADDIT. FEE	

SMALL ENTITY TYPE <input type="checkbox"/>		OTHER THAN SMALL ENTITY <input type="checkbox"/>	
RATE	ADDITIONAL FEE	RATE	ADDITIONAL FEE
X3.9 =		X3.9 =	255.00
X42 =		X42 =	200.00
+140 =		+140 =	
TOTAL ADDIT. FEE		TOTAL ADDIT. FEE	455.00

FD-450 (Rev. 12/02)

U.S. Government Printing Office: 2003 - 498-278/09151

Patent and Trademark Office U.S. DEPARTMENT OF COMMERCE

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IFW

Practitioner's Docket No. 2002-IP-009210U1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of _____
Inventor(s)

for _____
Title of invention

OR

In re application of: Philip D. Nguyen, et al.

Application No.: 0 10/608,291

Group Art Unit: 3672

Filed: 6/27/2003

Examiner: unknown

For: COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK

PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUBTERRANEAN WELL

Mail Stop Amendment

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
WITHIN THREE MONTHS OF FILING OR
BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))**

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*

(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10 *

☒ with sufficient postage as first class mail.

☐ as "Express Mail Post Office to Addressee"

Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Chasidy Smith
Signature

Date: 10-2-05

Chasidy Smith

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 1 of 3)

NOTE: 37 C.F.R. 1.98(b):

(1) Each U.S. patent listed in an information disclosure statement must be identified by inventor, patent number, and issue date.

(2) Each U.S. patent application publication listed in an information disclosure statement shall be identified by applicant, patent application publication number, and publication date.

(3) Each U.S. application listed in an information disclosure statement must be identified by the inventor, application number, and filing date.

(4) Each foreign patent or published foreign patent application listed in an information disclosure statement must be identified by the country or patent office which issued the patent or published the application, an appropriate document number, and the publication date indicated on the patent or published application.

(5) Each publication listed in an information disclosure statement must be identified by publisher, author (if any), title, relevant pages of the publication, date, and place of publication.

WARNING: No extension of time can be had under 37 C.F.R. § 1.136 (a) or (b) for filing an IDS. 37 C.F.R. § 1.97(f).

NOTE: The "filing date of a national application" under 37 C.F.R. § 1.97(b) has two possible meanings. Where the filing is a direct one to the United States Patent & Trademark Office, the filing is defined in 37 C.F.R. § 1.53(b) as "the date on which: (1) A specification containing a description pursuant to § 1.71 and at least one claim pursuant to § 1.75; and (2) any drawing required by § 1.81(a), are filed in the Patent and Trademark Office in the name of the actual inventor or inventors as required by § 1.41." 37 C.F.R. § 1.97(b)(1). On the other hand, an international application that enters the national stage occurs when the applicant has filed the documents and fees required by 35 U.S.C. § 371(c) within the periods set forth in § 1.494 or § 1.495. 35 U.S.C. § 371(c) requires the filing of the following: (1) the basic national fee; (2) a copy of the international application, unless already sent by the International Bureau, and optionally an English translation if filed in another language; and, also optionally (3) amendments under PCT Article 19, with a translation into English if made in another language; (4) an oath or declaration; and (5) a translation into English of any annexes to the international preliminary examination report, if such annexes were made in another language. The optional items must be submitted later, with surcharges. 37 C.F.R. § 1.97(b)(2).

IDENTIFICATION OF TIME OF FILING THE ACCOMPANYING INFORMATION DISCLOSURE STATEMENT

The information disclosure statement submitted herewith is being filed within three months of the filing date of the application or date of entry into the national stage of an international application or before the mailing date of a first Office action on the merits, whichever event occurs last. 37 C.F.R. § 1.97(b).

NOTE: "No certification or fee is due when the filing is made within the above time period. It is advisable to ensure that no Office action has been mailed if the disclosure statement is delayed until after three months from filing."

NOTE: "An information disclosure statement will be considered to have been filed on the day it was received in the Office, or on an earlier date of a mailing if accompanied by a properly executed certificate of mailing under 37 C.F.R. 1.8, or Express Mail certificate under 37 C.F.R. 1.10. An Office action is mailed on the date indicated in the Office action." Notice of April 20, 1992 (1138 O.G. 37-41, 39). See also § 609, M.P.E.P., 8th Edition.

NOTE: "The term 'national application' includes continuing applications (continuations, divisions, continuations-in-part) so three-months will be measured from the actual filing date of an application as opposed (sic) to the effective date of a continuing application." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [6-3]—page 2 of 3)

NOTE: "An action on the merits means an action which treats the patentability of the claims in an application, as opposed to only formal or procedural requirements. An action on the merits would, for example, contain a rejection or indication of allowability of a claim or claims rather than just a restriction requirements (37 C.F.R. 1.142) or just a requirement for additional fees to have a claim considered (37 C.F.R. 1.16(d)). Thus, if an application was filed on Jan. 1 and the first Office action on the merits was not mailed until six months later on July 1, the examiner would be required to consider any proper information disclosure statement filed prior to July 1." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

WARNING: "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1992 (1141 O.G. 63). But see § 103(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(d) and in a request for continued examination (RCE) under § 1.114.

Reg. No.: 28,626

Tel. No.: (580)-251-3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

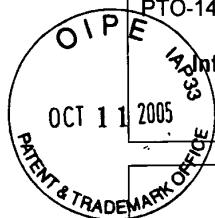
(type or print name of practitioner)

PO BOX 1431

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DUNCAN OK 73536-0440

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [6-3]—page 3 of 3)



PTO-1449 Information Disclosure Citation in an Application	Application No. 10/608,291	Applicant(s): Philip D. Nguyen, et al.	
	Docket Number 2002-IP-009210U1	Group Art Unit 3672	Filing Date 06/27/2003

U.S. PATENT DOCUMENTS

		DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE

NON-PATENT DOCUMENTS

		DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE
		Cordes, et al., <i>Mechanism and Catalysis for Hydrolysis of Acetals, Ketals, and Other Esters</i> , Department of Chemistry, Indiana University, Bloomington, Indiana, Chemical Reviews, 1974, Vol. 74, No. 5, pp. 581-603	
		TODD, ET AL., A CHEMICAL "TRIGGER" USEFUL FOR OILFIELD APPLICATIONS, SOCIETY OF PETROLEUM ENGINEERS, INC., SPE 92709	02/04/05

EXAMINER	DATE CONSIDERED
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.	



Application Serial No. 10/608,291
Attorney Docket No. 2002-IP-009210U1

THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
NGUYEN *ET AL.*

Serial No.: 10/608,291

Filed: June 27, 2003

Title: "COMPOSITIONS AND METHODS FOR
IMPROVING PROPPANT PACK
PERMEABILITY AND FRACTURE
CONDUCTIVITY IN A SUBTERRANEAN
WELL"

§
§ Group Art Unit: 3672
§
§
§ Examiner: SUCHFIELD, GEORGE A.
§
§
§ Atty. Docket No: 2002-IP-009210U1
§
§
§
§
§

MAIL STOP AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, Va 22313-1450

CERTIFICATE OF MAILING VIA EXPRESS MAIL	
ATTY. DOCKET No.: 2002-IP-009210U1	
GROUP ART UNIT: 3672	
EXAMINER: SUCHFIELD, GEORGE A.	
PURSUANT TO 37 C.F.R. § 1.10, I HEREBY CERTIFY THAT I HAVE INFORMATION AND A REASONABLE BASIS FOR BELIEF THAT THIS CORRESPONDENCE WILL BE DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS EXPRESS MAIL, POST OFFICE TO ADDRESSEE, ON THE DATE INDICATED BELOW, AND IS ADDRESSED TO:	
MAIL STOP AMENDMENT HONORABLE COMMISSIONER FOR PATENTS P.O. Box 1450 ALEXANDRIA, VA 22313-1450.	
TAMMY KNIGHT	9/7/05 DATE
EXPRESS MAIL LABEL: ED684784173US	

**AMENDMENT AND RESPONSE UNDER 37 C.F.R. § 1.111 TO
NON-FINAL OFFICE ACTION, MAILED MAY 17, 2005**

Sir:

In response to the Office Action mailed on May 17, 2005 (the "Office Action"), please amend the above-identified application as follows:

- **Amendments to the Claims** are reflected in the listing of claims that begins on page 3 of this paper.

09/12/2005 MAHKED1 00000070 080300 10608291

01 FC:1251

120.00 DA

Page 1

Response to Office Action Mailed May 17, 2005

- **Remarks/Arguments** begin on page 11 of this paper.
- **Summary and Petition for Extension of Time to File this Response** begins on page 22 of this paper.

AMENDMENTS TO THE CLAIMS

This listing of claims will replace all prior versions, and listings, of claims in the application:

Claims:

1. (Currently Amended) A method of increasing the conductivity of a fracture in a subterranean formation comprising the steps of:
providing a fracturing treatment fluid comprising a proppant composition, the proppant composition comprising proppant particulates and a degradable material ~~capable of undergoing an irreversible degradation downhole that comprises one or more poly(orthoesters);~~
introducing the proppant composition to the fracture; and
allowing the proppant composition to form a proppant matrix having voids in the fracture.
2. (Currently Amended) The method of claim 1 wherein the proppant particulates ~~comprise~~ are selected from the group consisting of sand, walnut hulls, or man-made proppant particulates, and combinations thereof.
3. (Previously Presented) The method of claim 1 wherein the proppant particulates have a size of about 10 to about 60 US mesh.
4. (Original) The method of claim 1 wherein the proppant composition further comprises a curable resin, a tackifying agent, or both.
5. (Currently Amended) The method of claim 4 wherein the curable resin ~~comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin~~ is selected from the group consisting of epoxies, furans, phenolics, furfuryl aldehydes, furfuryl alcohols, and combinations thereof.
6. (Previously Presented) The method of claim 1 wherein the proppant composition comprises interlocking proppant particulates.
7. (Currently Amended) The method of claim 1 wherein the degradable material further comprises a degradable polymer or a dehydrated salt.
8. (Currently Amended) The method of claim 7 wherein the degradable polymer comprises a second degradable material selected from the group consisting of polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly(ϵ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(amino

~~acids), poly(ethylene oxides), polyphosphazenes, and combinations thereof a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(ε-caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amine acid), a poly(ethylene oxide), or a polyphosphazene.~~

9. (Original) The method of claim 1 wherein the degradable material further comprises a plasticizer.

10. (Original) The method of claim 7 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

11. (Currently Amended) The method of claim 1 wherein the degradable material further comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

12. (Currently Amended) The method of claim 1 wherein the degradable material further comprises a stereoisomer of a poly(lactide).

13. (Previously Presented) The method of claim 1 wherein the proppant composition comprises a poly(lactic acid) degradable material and bauxite proppant particulates, the bauxite proppant particulates at least partially coated with a curable epoxy resin.

14. (Original) The method of claim 1 wherein the degradable material is present in the proppant composition in an amount sufficient to create a desirable number of voids in the proppant matrix.

15. (Original) The method of claim 1 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the composition.

16. (Currently Amended) The method of claim 1 wherein the degradable material further comprises particles having a rod-like shape.

17. (Currently Amended) The method of claim 1 wherein the degradable material further comprises an inorganic or organic compound.

18. (Currently Amended) The method of claim 17 wherein the inorganic or organic compound ~~comprises~~ is selected from the group consisting of sodium acetate trihydrate, L-tartaric acid disodium, salt dihydrate, sodium citrate dihydrate, hydrate of an inorganic acid, hydrate of an inorganic acid salt, sodium tetraborate decahydrate, sodium hydrogenphosphate

heptahydrate, sodium phosphate, dodecahydrate, amylose, starch-based hydrophilic ~~polymer polymers, or a cellulose-based hydrophilic polymer polymers, and combinations thereof.~~

19. (Original) The method of claim 1 wherein the degradable material is a composite.

20. (Currently Amended) A method of enhancing the permeability of a proppant matrix comprising the step of introducing a plurality of voids into the proppant matrix by a degradation of a degradable material that comprises one or more poly(orthoesters) within the proppant matrix.

21. (Currently Amended) The method of claim 20 wherein the proppant matrix comprises a material selected from the group consisting of sand, walnut hulls, or man-made proppant particulates, and combinations thereof.

22. (Original) The method of claim 20 wherein the proppant matrix comprises a curable resin, a tackifying agent, or both.

23. (Currently Amended) The method of claim 22 wherein the curable resin ~~comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin~~ is selected from the group consisting of epoxies, furans, phenolics, furfuryl aldehydes, furfuryl alcohols, and combinations thereof.

24. (Original) The method of claim 20 wherein the proppant matrix comprises interlocking proppant particulates.

25. (Currently Amended) The method of claim 20 wherein the degradable material further comprises a degradable polymer or a dehydrated salt.

26. (Currently Amended) The method of claim 25 wherein the degradable polymer ~~comprises~~ is selected from the group consisting of polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly(ϵ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(amino acids), poly(ethylene oxides), polyphosphazenes, and combinations thereof ~~a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly(ϵ -caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amino acid), a poly(ethylene oxide), or a polyphosphazene.~~

27. (Original) The method of claim 20 wherein the degradable material further comprises a plasticizer.

28. (Currently Amended) The method of claim 25 wherein the dehydrated salt ~~comprises~~ is selected from the group consisting of anhydrous sodium tetraborate, ~~or~~ anhydrous boric acid, and combinations thereof.

29. (Currently Amended) The method of claim 20 wherein the degradable material further comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

30. (Currently Amended) The method of claim 20 wherein the degradable material further comprises a stereoisomer of a poly(lactide).

31. (Currently Amended) The method of claim 20 wherein the proppant matrix comprises a poly(lactic acid) degradable material and bauxite proppant particulates, the bauxite proppant particulates being at least partially coated with a curable epoxy resin.

32. (Original) The method of claim 20 wherein the degradable material is present in the proppant matrix in an amount sufficient to create a desirable number of voids in the proppant matrix.

33. (Currently Amended) The method of claim 20 wherein the degradable material is present in the proppant matrix composition in an amount of about 0.1% to about 30% by weight of the proppant matrix particulates in the composition.

34. (Original) The method of claim 20 wherein the degradable material comprises particles having a rod-like shape.

35. (Currently Amended) The method of claim 20 wherein ~~the~~ at least a portion of the voids in the proppant matrix are channel-like in shape.

36. (Original) The method of claim 20 wherein the proppant matrix has a conductivity equal to or greater than 4500 darcies at a pressure of about 2000 psi.

37. (Original) The method of claim 20 wherein the proppant matrix has a conductivity equal to or greater than 4500 darcies at a pressure of about 4000 psi.

38. (Original) The method of claim 20 wherein the proppant matrix has a conductivity equal to or greater than 4000 darcies at a pressure of about 6000 psi.

39. - 72. (Cancelled)

73. (New) A method of increasing the conductivity of a fracture in a subterranean formation comprising the steps of:

providing a fracturing treatment fluid comprising a proppant composition, the proppant composition comprising proppant particulates and a degradable composite material;
introducing the proppant composition to the fracture; and
allowing the proppant composition to form in the fracture a proppant matrix having voids.

74. (New) The method of claim 73 wherein the proppant particulates are selected from the group consisting of sand, walnut hulls, man-made proppant particulates, and combinations thereof.

75. (New) The method of claim 73 wherein the proppant particulates have a size of about 10 to about 60 US mesh.

76. (New) The method of claim 73 wherein the proppant composition further comprises a curable resin, a tackifying agent, or both.

77. (New) The method of claim 76 wherein the curable resin is selected from the group consisting of epoxies, furans, phenolics, furfuryl aldehydes, furfuryl alcohols, and combinations thereof.

78. (New) The method of claim 73 wherein the proppant composition comprises interlocking proppant particulates.

79. (New) The method of claim 73 wherein the degradable composite material further comprises a degradable polymer or a dehydrated salt.

80. (New) The method of claim 79 wherein the degradable polymer is selected from the group consisting of polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly(ϵ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(amino acids), poly(ethylene oxides), polyphosphazenes, and combinations thereof.

81. (New) The method of claim 79 wherein the dehydrated salt is selected from the group consisting of anhydrous sodium tetraborate or anhydrous boric acid, and combinations thereof.

82. (New) The method of claim 73 wherein the degradable composite material further comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

83. (New) The method of claim 73 wherein the degradable composite material further comprises a stereoisomer of a poly(lactide).

84. (New) The method of claim 73 wherein the proppant composition comprises a poly(lactic acid) degradable material and bauxite proppant particulates, the bauxite proppant particulates being at least partially coated with a curable epoxy resin.

85. (New) The method of claim 73 wherein the degradable composite material is present in the proppant composition in an amount sufficient to create a desirable number of voids in the proppant matrix.

86. (New) The method of claim 73 wherein the degradable composite material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the composition.

87. (New) The method of claim 73 wherein the degradable composite material further comprises particles having a rod-like shape.

88. (New) The method of claim 73 wherein the degradable composite material further comprises an inorganic or organic compound.

89. (New) The method of claim 88 wherein the inorganic or organic compound is selected from the group consisting of sodium acetate trihydrate, L-tartaric acid disodium, salt dihydrate, sodium citrate dihydrate, hydrate of an inorganic acid, hydrate of an inorganic acid salt, sodium tetraborate decahydrate, sodium hydrogenphosphate heptahydrate, sodium phosphate, dodecahydrate, amylose, starch-based hydrophilic polymers, cellulose-based hydrophilic polymers, and combinations thereof.

90. (New) A method of enhancing the permeability of a proppant matrix comprising the step of introducing a plurality of voids into the proppant matrix by a degradation of a degradable composite material within the proppant matrix.

91. (New) The method of claim 90 wherein the proppant matrix comprises a material selected from the group consisting of sand, walnut hulls, man-made proppant particulates, and combinations thereof.

92. (New) The method of claim 90 wherein the proppant matrix comprises a curable resin, a tackifying agent, or both.

93. (New) The method of claim 92 wherein the curable resin is selected from the group consisting of epoxies, furans, phenolics, furfuryl aldehydes, furfuryl alcohols, and combinations thereof.

94. (New) The method of claim 90 wherein the proppant matrix comprises interlocking proppant particulates.

95. (New) The method of claim 90 wherein the degradable composite material further comprises a degradable polymer or a dehydrated salt.

96. (New) The method of claim 95 wherein the degradable polymer is selected from the group consisting of polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly(ϵ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(amino acids), poly(ethylene oxides), polyphosphazenes, and combinations thereof.

97. (New) The method of claim 96 wherein the dehydrated salt is selected from the group consisting of anhydrous sodium tetraborate, anhydrous boric acid, and combinations thereof.

98. (New) The method of claim 90 wherein the degradable composite material further comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

99. (New) The method of claim 90 wherein the degradable composite material further comprises a stereoisomer of a poly(lactide).

100. (New) The method of claim 90 wherein the proppant matrix comprises a poly(lactic acid) degradable material and bauxite proppant particulates, the bauxite proppant particulates being at least partially coated with a curable epoxy resin.

101. (New) The method of claim 90 wherein the degradable material is present in the proppant matrix in an amount sufficient to create a desirable number of voids in the proppant matrix.

102. (New) The method of claim 90 wherein the degradable composite material is present in the proppant matrix in an amount of about 0.1% to about 30% by weight of the proppant matrix.

103. (New) The method of claim 90 wherein the degradable composite material comprises particles having a rod-like shape.

104. (New) The method of claim 90 wherein at least a portion of the voids in the proppant matrix are channel-like in shape.

105. (New) The method of claim 90 wherein the proppant matrix has a conductivity equal to or greater than 4500 darcies at a pressure of about 2000 psi.

106. (New) The method of claim 90 wherein the proppant matrix has a conductivity equal to or greater than 4500 darcies at a pressure of about 4000 psi.

107. (New) The method of claim 90 wherein the proppant matrix has a conductivity equal to or greater than 4000 darcies at a pressure of about 6000 psi.

REMARKS / ARGUMENTS

I. General Remarks and Remarks Regarding the Restriction Requirement

Please consider the application in view of the following remarks.

During a telephone conversation with the Examiner on May 4, 2005, claims 1-38 were provisionally elected in response to the Examiner's restriction requirement. This provisional election is hereby confirmed and claims 39-72 have been cancelled. No amendment to inventorship is necessitated by this election. Applicants respectfully reserve the right to present the cancelled claims in one or more divisional applications.

II. Disposition of Claims

Claims 1-38 and 73-107 are pending in this application.

Claims 1, 2, 5, 7, 8, 11, 12, 16-18, 20, 21, 23, 25, 26, 28-31, 33, and 35 have been amended to more clearly claim the present invention. These amendments add no new matter to the application, and are supported by the specification as filed.

Claims 73-107 are new. These new claims add no new matter to the application, and are supported by the specification as filed.

Claims 14 and 32 stand rejected under 35 U.S.C. § 112. Claims 1, 2, 7-9, 12, 14, 16, 17-21, 25-27, 30, 32, 34 and 35 stand rejected under 35 U.S.C. § 102(a). Claims 1-5, 7, 8, 14, 15, 17, 19-23, 25, 26, 32, 33, and 35 stand rejected under 35 U.S.C. § 102(b). Claims 3, 9, 12, 13, 15, 27, 30, 31, 33, and 36-38 stand rejected under 35 U.S.C. § 103(a). The Examiner has objected to claims 6, 10, 11, 16, 24, 28, 29, and 34.

III. Rejections of Claims Under § 112

Claims 14 and 32 stand rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicants regard as the invention. Applicants respectfully traverse.

With respect to this rejection, the Examiner writes that "[c]laims 14 and 32 are deemed indefinite with respect to the recitation of 'a desirable number of voids' [since] the term 'desirable' is subjective or non-specific." (*See* Office Action at ¶ 8.) Applicants respectfully submit that this term is sufficiently definite to comply with 35 U.S.C. § 112. "The fact that claim language . . . may not be precise, does not automatically render the claim indefinite under 35 U.S.C. § 112, second paragraph. Acceptability of the claim language depends on whether one of ordinary skill in the art would understand what is claimed, in light of the specification." *See*

MANUAL OF PATENT EXAMINING PROCEDURE § 2173.05(b) (citations omitted). For example, a limitation such as “an effective amount” has been held to be sufficiently definite when read in light of the supporting disclosure and in the absence of any prior art which would give rise to uncertainty about the scope of the claim. *See* MANUAL OF PATENT EXAMINING PROCEDURE § 2173.05(c) (citing *Ex parte Skuballa*, 12 U.S.P.Q.2d 1570 (Bd. Pat. App. & Inter. 1989)). Here, Applicants are aware of no prior art that would create any uncertainty as to the scope of the subject claims. Rather, one of ordinary skill in the art readily would ascertain, in light of Applicants’ disclosure, that “a desirable number of voids” (as recited in claims 14 and 32) is a number of voids effective to accomplish the objectives of that particular use from among those described in the specification or known in the art. Accordingly, Applicants respectfully assert that the use of the term “desirable” in the subject claims satisfies the requirements of 35 U.S.C. § 112, second paragraph, and respectfully request the withdrawal of these rejections.

IV. Rejections of Claims Over *Cooke I*

A. Rejections of Claims Over *Cooke I* Under § 102(a)

Claims 1, 2, 7-9, 12, 14, 16-21, 25-27, 30, 32, 34, and 35 stand rejected under 35 U.S.C. § 102(a) as being anticipated by U.S. Patent Application Publication No. 2003/0060374 by Cooke, Jr. (“*Cooke I*”). With respect to this rejection, the Examiner writes:

[*Cooke I*] (note Figure 2c) may employ a proppant composition in the fracturing process comprising a mixture or composite of proppant particulates and a degradable polymer, as called for in independent claims 1 and 20.

[*Cooke I*] further discloses one or more of the degradable polymers set forth in claims 8, 12, 18, 26 and 30 and may further use a plasticizer, as called for in claims 9 and 27.

As per claim 14 and 32 it appears from the illustration in Figure 2c that a “desirable” number of voids will be present [upon] degradation and removal of the degradable polymer phase.

As per claim 16 and 34, note that the proppant composition of Figure 2c of [*Cooke I*], and thus the degradable polymer component, appear to have a “rod-like” shape, as recited.

As per claim 35, it is deemed that the resulting void space(s) created by the degradation of the degradable polymer will necessarily be “channel-like” in shape, e.g., due to the accompanying or resulting fluid-flow through the proppant matrix.

(See Office Action at ¶ 10 (emphasis added).) Applicants respectfully disagree.

In order to form a basis for a rejection under 35 U.S.C. § 102(a), a prior art reference must disclose each and every element as set forth in the claim. MANUAL OF PATENT EXAMINING PROCEDURE § 2131 (2004). Applicants respectfully submit that *Cooke I* does not disclose each element as set forth in the rejected claims, as amended herein, since (1) *Cooke I* does not disclose degradable materials that comprise one or more poly(orthoesters) as recited in claims 1 and 20, as amended herein, and (2) *Cooke I* does not disclose degradable materials that are composites, as recited in claim 19. Therefore, those claims, and all claims dependent thereon, are allowable over *Cooke I*.

1. Rejections of Claims 1, 2, 7-9, 12, 14, 16, 17-21, 25-27, 30, 32, 34, and 35

Applicants respectfully submit that *Cooke I* does not anticipate claims 1, 2, 7-9, 12, 14, 16-21, 25-27, 30, 32, 34, and 35 since *Cooke I* does not disclose degradable materials that comprise one or more poly(orthoesters), as recited in claims 1 and 20, as amended herein. Although *Cooke I* does teach degradable materials that comprise “polyesters” (see *Cooke I* at ¶ 0023) for use in some contexts, Applicants respectfully submit that *Cooke I* does not disclose or teach poly(orthoesters), either explicitly or inherently, since poly(orthoesters) are not polyesters. Rather, the term “orthoester” is a misnomer, and orthoesters are actually understood in the art to be ethers based on their chemical structure and in view of their lack of base-catalyzed hydrolysis. See, e.g., Anton Skrabal & Otto Ringer, “The Hydrolysis Rate of Orthoformic Acid Ethyl Ether,” CHEMICAL INSTITUTE OF THE UNIVERSITY OF GRAZ, at 1 (January 13, 1921) (“According to its behavior during hydrolysis, . . . this substance and presumably also the analog compounds with the chemical group -C(OR)₃, where R signifies an alkyl, would be designated properly as ethers and not as esters.”) (An English translation of this reference is enclosed for the Examiner’s convenience.) Therefore, the disclosure of polyesters in *Cooke I* does not disclose or teach (explicitly or inherently) the use of poly(orthoesters), which are generally understood to be ethers. Applicants therefore respectfully assert that *Cooke I* does not disclose all elements of claims 1 and 20, as amended herein, and thus these claims are allowable over *Cooke I*. Moreover, since “a claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers,” and since claims 2, 7-9, 12, 14, 16-19, 21, 25-27, 30, 32, 34, and 35 depend, directly or indirectly, from claim 1 or 20, these

dependent claims are allowable for at least the same reasons. *See* 35 U.S.C. § 112 ¶ 4 (2004). Accordingly, Applicants respectfully request the withdrawal of these rejections.

2. Rejection of Claim 19

Applicants respectfully submit that *Cooke I* does not anticipate claim 19 since *Cooke I* does not disclose degradable materials that are composites. Although the Examiner asserts that *Cooke I* teaches “a mixture or composite of proppant particulates and a degradable polymer,” Applicants respectfully submit that *Cooke I* does not disclose or teach the use of a degradable material that is a composite, as that term is defined by Applicants in their disclosure. Applicants have explicitly defined the term “composite” to refer to a degradable material wherein “the degradable material [is] mixed with [an] inorganic or organic compound.” (*See* “Description of Preferred Embodiments” at ¶ 033.) *Cooke I* does not explicitly disclose a “composite” material, nor does it disclose any material that is formed according to the definition provided by Applicants. Applicants therefore respectfully assert that *Cooke I* does not disclose this element of claim 19, and thus this claim is allowable over *Cooke I*. Accordingly, Applicants respectfully request the withdrawal of this rejection.

B. Rejections of Claims Over *Cooke I* Under § 103(a)

Claims 3, 15, 33, and 36-38 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over *Cooke I*. With respect to this rejection, the Examiner writes that “[t]he size range of the proppant particles utilized in the methods of [*Cooke I*], as recited in claim 3,” the “resulting proppant matrix conductivity recited in claims 36-38,” and the “precise amount of degradable material present in the proppant composition utilized by [*Cooke I*], as called for in claims 15 and 33 . . . would have been an obvious matter of choice or design in carrying out the fracturing process of [*Cooke I*].” (*See* Office Action at ¶ 13.) To form a basis for a § 103(a) rejection, a prior art reference must teach or suggest each element in the claim. MANUAL OF PATENT EXAMINING PROCEDURE § 2142 (2004). However, as discussed in Section IV.A.1. above, *Cooke I* does not teach or suggest degradable materials that comprise one or more poly(orthoesters), as recited in claims 1 and 20, as amended herein. Since claims 3, 15, 33, and 36-38 depend, either directly or indirectly, on claim 1 or 20, they incorporate this limitation recited in claims 1 and 20, and thus *Cooke I* does not obviate dependent claims 3, 15, 33, and 36-38. Accordingly, Applicants respectfully request the withdrawal of these rejections.

V. Rejections of Claims Over *Betzold*

A. Rejections Over *Betzold* Under § 102(b)

Claims 1-5, 7, 8, 14, 15, 17, 19, 20, 22, 23, 25, 26, 32, 33, and 35 stand rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent No. 6,328,105 to Betzold ("*Betzold*"). With respect to this rejection, the Examiner writes:

[*Betzold*] (note col. 2, lines 33-62; col. 3, line 42 - col. 4, line 15) discloses a process of fracturing and propping a subterranean formation(s) with a proppant composition or composite especially in view of the coating on the proppant particles, comprising a mixture of a coated, bondable propping particles and removable particles, wherein such removable particles may decompose or degrade within the formation fracture, as called for in independent claims 1 and 20.

As per claim 3, the average particle size range set forth in the EXAMPLE of 800-1000 microns would appear to fall within the mesh particle size range recited.

As per claims 4, 5, 22 [and] 23, the conventional coated particles or coating formulations referred to in [*Betzold*] (note col. 3, lines 17-41) would appear to encompass those recited.

[*Betzold*] further discloses one or more of the degradable polymers set forth in claims 8 [and] 26.

As per claim 14 and 32 it is deemed that in the operation of the [*Betzold*] fracturing process, a "desirable" number of voids will be inherently or necessarily present upon degradation and removal of the degradable polymer phase, in order to allow flowback and production of mineral fluids.

As per claims 15 and 33, the exemplary range set forth in [*Betzold*] (note col. 5, lines 7-17) of 10-30% falls within the recited range of "0.1% to about 30%."

As per claim 35, it is deemed that the resulting void space(s) created by the degradation of the degradable polymer in the process of [*Betzold*] will necessarily be "channel-like" in shape, e.g., due to the accompanying or resulting fluid-flow through the proppant matrix.

(See Office Action at ¶ 14 (emphasis added).) Applicants respectfully traverse.

In order to form a basis for a rejection under 35 U.S.C. § 102(b), a prior art reference must disclose each and every element as set forth in the claim. MANUAL OF PATENT

EXAMINING PROCEDURE § 2131 (2004). Applicants respectfully submit that *Betzold* does not disclose each element as set forth in the rejected claims, as amended herein, since (1) *Betzold* does not disclose degradable materials that comprise one or more poly(orthoesters) as recited in claims 1 and 20, as amended herein, and (2) *Betzold* does not disclose degradable materials that are composites, as recited in claim 19. Therefore, those claims, and all claims dependent thereon, are allowable over *Betzold*.

1. Rejections of Claims 1-5, 7, 8, 14, 15, 17, 19, 20, 22, 23, 25, 26, 32, 33, and 35

Applicants respectfully submit that *Betzold* does not anticipate claims 1-5, 7, 8, 14, 15, 17, 19, 20, 22, 23, 25, 26, 32, 33, and 35 since *Betzold* does not disclose degradable materials that comprise one or more poly(orthoesters), as recited in claims 1 and 20, as amended herein. Although *Betzold* does teach removable materials that may decompose or degrade that comprise “polyester polymers” (see *Betzold* at col. 3, ll. 50-53) for use in some contexts, Applicants respectfully submit that *Betzold* does not disclose or teach poly(orthoesters), either explicitly or inherently, since poly(orthoesters) are not polyesters. Rather, as discussed above, the term “orthoester” is a misnomer, and orthoesters are understood in the art to be ethers based on their chemical structure and in view of their lack of base-catalyzed hydrolysis. See, e.g., Anton Skrabal & Otto Ringer, “The Hydrolysis Rate of Orthoformic Acid Ethyl Ether,” CHEMICAL INSTITUTE OF THE UNIVERSITY OF GRAZ, at 1 (January 13, 1921) (An English translation of this reference is enclosed for the Examiner’s convenience.) Therefore, the disclosure of polyesters in *Betzold* does not disclose or teach (explicitly or inherently) the use of poly(orthoesters), which are generally understood to be ethers. Applicants therefore respectfully assert that *Betzold* does not disclose all elements of claims 1 and 20, as amended herein, and thus these claims are allowable over *Betzold*. Moreover, since “a claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers,” and since claims 2-5, 7, 8, 14, 15, 17, 19, 22, 23, 25, 26, 32, 33, and 35 depend, directly or indirectly, from claim 1 or 20, these dependent claims are allowable for at least the same reasons. See 35 U.S.C. § 112 ¶ 4 (2004). Accordingly, Applicants respectfully request the withdrawal of these rejections.

2. Rejection of Claim 19

Applicants respectfully submit that *Betzold* does not anticipate claim 19 since *Betzold* does not disclose degradable materials that are composites. Although the Examiner

asserts that *Betzold* teaches “a proppant composition or composite” (e.g., coated proppant particles), Applicants respectfully submit that *Betzold* does not disclose or teach the use of a degradable material that is a composite, as that term is defined by Applicants in their disclosure. Applicants have explicitly defined the term “composite” to refer to a degradable material wherein “the degradable material [is] mixed with [an] inorganic or organic compound.” (See “Description of Preferred Embodiments” at ¶ 033.) *Betzold* does not explicitly disclose a “composite” material, nor does it disclose any material that is formed according to the definition provided by Applicants. Applicants therefore respectfully assert that *Betzold* does not disclose this element of claim 19, and thus this claim is allowable over *Betzold*. Accordingly, Applicants respectfully request the withdrawal of this rejection.

B. Rejections Over *Betzold* Under § 103(a)

Claims 36-38 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over *Betzold*. With respect to this rejection, the Examiner writes that “[t]o provide resulting proppant matrix conductivity recited in claims 36-38 would have been an obvious matter of choice or design in carrying out the fracturing process of [*Betzold*].” (See Office Action at ¶ 15.) To form a basis for a § 103(a) rejection, a prior art reference must teach or suggest each element in the claim. MANUAL OF PATENT EXAMINING PROCEDURE § 2142 (2004). However, as discussed in Section V.A.1. above, *Betzold* does not teach or suggest degradable materials that comprise one or more poly(orthoesters), as recited in claim 20, as amended herein. Since claims 36-38 depend, either directly or indirectly, on claim 20, they incorporate this limitation recited in claim 20, and thus *Betzold* does not obviate dependent claims 36-38. Accordingly, Applicants respectfully request the withdrawal of these rejections.

VI. Rejections of Claims Over *Betzold* in View of *Cooke I*

Claims 9, 12, 27, and 30 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over *Betzold* in view of *Cooke I*. With respect to claims 9 and 27, the Examiner writes that “it would have been obvious to one of ordinary skill in the art to which the invention pertains to employ a degradable polymer which further comprises a plasticizer and/or which has been plasticized in the proppant composition utilized in the fracturing and propping process of [*Betzold*], as taught by [*Cooke I*] (note para [0027]).” (See Office Action at ¶ 16.) With respect to claims 12 and 30, the Examiner writes that “it would have been obvious to one of ordinary skill in the art to which the invention pertains “to employ a poly(lactide) as the degradable

polymer in the proppant composition utilized in the fracturing and propping process of [*Betzold*], as taught by [*Cooke I*] (note para [0023]).” (See Office Action at ¶ 16.) To form a basis for a § 103(a) rejection, a combination of prior art references must teach or suggest each element in the claim. MANUAL OF PATENT EXAMINING PROCEDURE § 2142 (2004). However, as discussed in Sections IV.A.1. and V.A.1. above, neither *Cooke I* nor *Betzold* teaches or suggests degradable materials that comprise one or more poly(orthoesters), as recited in claims 1 and 20, as amended herein. Since claims 9, 12, 27, and 30 depend, either directly or indirectly, on claim 1 or 20, they incorporate this limitation recited in claims 1 and 20, and thus the combination of *Cooke I* and *Betzold* does not obviate dependent claims 9, 12, 27, and 30. Accordingly, Applicants respectfully request the withdrawal of these rejections.

VII. Rejections of Claims Over *Betzold* in View of *Cooke I* and *Cooke II*

Claims 13 and 31 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over *Betzold* in view of *Cooke I* and U.S. Patent No. 4,068,718 to Cooke, Jr. *et al.* (“*Cooke II*”). With respect to this rejection, the Examiner writes that “it would have been obvious to one of ordinary skill in the art to which the invention pertains to employ a poly(lactide) as the degradable polymer in the proppant composition utilized in the fracturing and propping process of [*Betzold*], as taught by [*Cooke I*] (note para [0023]),” and “[i]t would also have been obvious to employ bauxite as the proppant particles in the process of [*Betzold*], as taught by [*Cooke II*] (note col. 2, lines 13-34).” (See Office Action at ¶ 17.) To form a basis for a § 103(a) rejection, a combination of prior art references must teach or suggest each element in the claim. MANUAL OF PATENT EXAMINING PROCEDURE § 2142 (2004). However, as discussed in Sections IV.A.1. and V.A.1. above, neither *Cooke I* nor *Betzold* teaches or suggests degradable materials that comprise one or more poly(orthoesters), as recited in claims 1 and 20, as amended herein. Nor does *Cooke II* teach or suggest degradable materials that comprise that comprise one or more poly(orthoesters). Rather, *Cooke II* only discloses the use of proppant particulates composed of sintered bauxite, and does not discuss the use of degradable materials at all. (See *Cooke II* at col. 2, ll. 16-22.) Since claims 13 and 31 depend, either directly or indirectly, on claim 1 or 20, they incorporate this limitation recited in claims 1 and 20, and thus the combination of *Betzold*, *Cooke I*, and *Cooke II* does not obviate dependent claims 13 and 31. Accordingly, Applicants respectfully request the withdrawal of these rejections.

VIII. Rejections of Claims over *Atkins*

A. Rejections Over *Atkins* Under § 102(b)

Claims 1, 3, 7, 14, 17, 19, 20, 21, 25, 32, and 35 stand rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent No. 3,364,995 to Atkins *et al.* ("*Atkins*"). With respect to this rejection, the Examiner writes:

[*Atkins*] (note col. 4, line 64 - col. 5, line 2) discloses a process of fracturing and propping a subterranean formation(s) employing a proppant composition in the fracturing fluid which comprises a mixture or composite of proppant particulate and a degradable material, such as a solid spacer material which chemically decomposes in the fracture(s), as called for in independent claims 1 and 20.

As per claim 3, the recited range of 10-60 mesh falls within or is encompassed by the proppant size range in [*Atkins*] (note col. 2, lines 33-57) of 4-80 mesh.

As per claims 7 and 25, [*Atkins*] may employ either a degradable polymer, i.e., a polysulfone and a dehydrated salt, such as a carbonate as the degradable component in the proppant mixture.

As per claims 14 and 32, it is deemed that in the operation of the [*Atkins*] fracturing process, a "desirable" number of voids will be inherently or necessarily present upon degradation and removal of the degradable polymer phase, in order to allow flowback and production of mineral fluids.

As per claim 35, it is deemed that the resulting void space(s) created by the degradation of the degradable polymer in the process of [*Atkins*] will necessarily be "channel-like" in shape, e.g., due to the accompanying or resulting fluid-flow through the proppant matrix.

(See Office Action at ¶ 18 (emphasis added).) Applicants respectfully traverse.

In order to form a basis for a rejection under 35 U.S.C. § 102(b), a prior art reference must disclose each and every element as set forth in the claim. MANUAL OF PATENT EXAMINING PROCEDURE § 2131 (2004). Applicants respectfully submit that *Atkins* does not disclose each element as set forth in the rejected claims, as amended herein, since (1) *Atkins* does not disclose degradable materials that comprise one or more poly(orthoesters) as recited in claims 1 and 20, as amended herein, and (2) *Atkins* does not disclose degradable materials that

are composites, as recited in claim 19. Therefore, those claims, and all claims dependent thereon, are allowable over *Atkins*.

1. Rejections of Claims 1, 3, 7, 14, 17, 19, 20, 21, 25, 32, and 35

Applicants respectfully submit that *Atkins* does not anticipate claims 1, 3, 7, 14, 17, 19, 20, 21, 25, 32, and 35 since *Atkins* does not disclose degradable materials that comprise one or more poly(orthoesters), as recited in claims 1 and 20, as amended herein. Rather, *Atkins* only teaches the use of spacer materials that comprise carbonates, polysulfones, carbides, or ammonium salts with a water soluble hydroxide. (See *Atkins* at col. 2, ll. 58-65.) Applicants therefore respectfully assert that *Atkins* does not disclose all elements of claims 1 and 20, as amended herein, and thus these claims are allowable over *Atkins*. Moreover, since “a claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers,” and since claims 3, 7, 14, 17, 19, 21, 25, 32, and 35 depend, directly or indirectly, from claim 1 or 20, these dependent claims are allowable for at least the same reasons. See 35 U.S.C. § 112 ¶ 4 (2004). Accordingly, Applicants respectfully request the withdrawal of these rejections.

2. Rejection of Claim 19

Applicants respectfully submit that *Atkins* does not anticipate claim 19 since *Atkins* does not disclose degradable materials that are composites. Although the Examiner asserts that *Atkins* teaches “a mixture or composite of proppant particulates and a degradable material,” Applicants respectfully submit that *Atkins* does not disclose or teach the use of a degradable material that is a composite, as that term is defined by Applicants in their disclosure. Applicants have explicitly defined the term “composite” to refer to a degradable material wherein “the degradable material [is] mixed with [an] inorganic or organic compound.” (See “Description of Preferred Embodiments” at ¶ 033.) *Atkins* does not explicitly disclose a “composite” material, nor does it disclose any material that is formed according to the definition provided by Applicants. Applicants therefore respectfully assert that *Atkins* does not disclose this element of claim 19, and thus this claim is allowable over *Atkins*. Accordingly, Applicants respectfully request the withdrawal of this rejection.

B. Rejections Over *Atkins* Under § 103(a)

Claims 36-38 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over *Atkins*. With respect to this rejection, the Examiner writes that “[t]o provide resulting proppant

matrix conductivity recited in claims 36-38 would have been an obvious matter of choice or design in carrying out the fracturing process of [*Atkins*].” (See Office Action at ¶ 15.) To form a basis for a § 103(a) rejection, a prior art reference must teach or suggest each element in the claim. MANUAL OF PATENT EXAMINING PROCEDURE § 2142 (2004). However, as discussed in Section VIII.A.1. above, *Atkins* does not teach or suggest degradable materials that comprise one or more poly(orthoesters), as recited in claims 1 and 20, as amended herein. Since claims 36-38 depend, either directly or indirectly, on claim 20, they incorporate this limitation recited in claim 20, and thus *Atkins* does not obviate dependent claims 36-38. Accordingly, Applicants respectfully request the withdrawal of these rejections.

IX. Objections to Claims

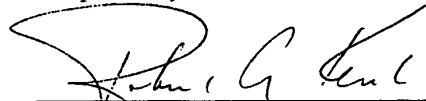
The Examiner has objected to claims 6, 10, 11, 16, 24, 28, 29, and 34 as being dependent upon a rejected base claim, but notes that these claims would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. Claims 6, 10, 11, 16, 24, 28, 29, and 34 each depend, either directly or indirectly, from independent claim 1 or 20. As Applicants have asserted herein that these independent claims, as amended, are allowable over the prior art of record, the withdrawal of the objections to dependent claims 6, 10, 11, 16, 24, 28, 29, and 34 is respectfully requested.

**SUMMARY AND PETITION FOR EXTENSION OF TIME OF ONE MONTH
TO FILE THIS RESPONSE**

In light of the above remarks, Applicants respectfully request reconsideration and withdrawal of the outstanding rejections. Applicants further submit that the application is now in condition for allowance, and earnestly solicit timely notice of the same. Should the Examiner have any questions, comments or suggestions in furtherance of the prosecution of this application, the Examiner is invited to contact the attorney of record by telephone, facsimile, or electronic mail.

Applicants hereby petition under the provisions of 37 C.F.R. §1.136(a) for a one-month extension of time to file this Response. The Commissioner is hereby authorized to debit the Deposit Account of Halliburton Energy Services, Inc., No. 08-0300 in the amount of \$120.00 for the corresponding fee under 37 C.F.R. §1.136(a). Applicants believe that there are no additional fees due in association with the filing of this Response. However, should the Commissioner deem that any additional fees are due, including any fees for extensions of time, Applicants respectfully request that the Commissioner accept this as a Petition Therefor, and direct that any additional fees be charged to the Deposit Account of Halliburton Energy Services, Inc., No. 08-0300.

Respectfully submitted,



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Date: September 7, 2005

Anton Skrabal¹, Otto Ringer¹: The hydrolysis rate of orthoformic acid ethyl ether

¹ Chemical Institute of the University of Graz.
Presented at the meeting of January 13, 1921.

Job No.: 415-104489

Ref.: 2004-014178U1

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THE HYDROLYSIS RATE OF ORTHOFORMIC ACID ETHYL ETHER

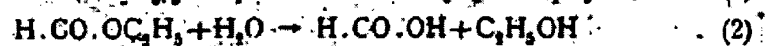
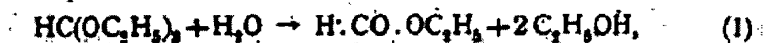
Introduction

Chemical kinetics research is still far removed from knowing the time course of simple hydrolytic reactions of the various substance classes with an ethereal bonded oxygen atom. Up to now, orthocarboxylic acid esters, which are connected with important constitution problems and synthetic methods, have in no way been worked up with regard to the kinetics of their hydrolysis.

A beginning will be made here with esters of the simplest orthocarboxylic acid, the hypothetical orthoformic acid, and the hydrolysis of its ester that is most easily accessible, orthoformic acid ethyl ester $\text{HC}(\text{OC}_2\text{H}_5)_3$, will be investigated. According to its behavior during hydrolysis, which is the result of the investigation under consideration, this substance and presumably also the analog compounds with the chemical group $-\text{C}(\text{OR})_3$, where R signifies an alkyl, would be designated properly as ethers and not as esters, with this more proper designation already being selected in the title.

From the rather comprehensive preparative literature available regarding this compound and the closest homolog, orthoacetic acid ether, it was then possible to find a criterion satisfactory enough to guide our work: during the hydrolysis--and we are still talking only about a hydrolysis brought about by acids--it was always possible to find, as degradation products, only bodies with an alkoxy group--namely, esters of the usual concerned acids--that is, formic acid, or acetic acid esters, or their decomposition products, acid and alcohol.

It should therefore be assumed that the hydrolysis of orthoformic acid ether would be calculated as a consecutive reaction with only one intermediate stage, in accordance with the following reaction equations:



--an assumption also confirmed by the experiment.

The rate of the second reaction, the saponification of the formic acid ester, in its dependence on the concentration of the ester and the ions H^+ and OH^- of the water, is already known [1]. Therefore, one had to determine the rate of the first reaction. According to explanations made by R. Wegscheider [2], it was basically the determination of the constants of three secondary reactions, the aqueous saponification, the alkaline saponification, and the acidic saponification, in which constants--since the work was carried out in aqueous solution--it is possible to include the constant water concentration.

As regards the analysis feasibility of the reaction mixture as a prerequisite for the feasibility measuring of the reaction and the change in acidity, which occurs as a result of the

reaction course and which influences the saponification rate, one can say the following. The first of the two secondary effects takes place without an "acid toning"; its course therefore changes nothing in the rate of the acidic and alkaline saponification. The second reaction releases an acid; its course therefore delays the alkaline saponification and favors the acidic saponification. The conversion after the second reaction results from the titration of the produced formic acid; the conversion after the first reaction, from the produced formic acid and the produced formic acid ester. The latter can be calculated accurately and quickly thanks to its very rapid alkaline saponification, by excess alkali, which saponifies it, and back-titration with acid. The prerequisite for the application feasibility of this analysis method is a corresponding resistance of ortho ethers with respect to alkali.

In order to test this assumption, we had to therefore first investigate the behavior of the ortho ether in a correspondingly alkaline medium.

The used orthoformic acid ethyl ether was a Kahlbaum preparation, always purified shortly before its use by fractional distillation. The measurements were carried out in a thermostat at 25°.

Therefore, the ortho ether was first introduced into a sodium carbonate solution and by titration of the soda with 0.1N HCL, relative to bicarbonate, the change in titer was determined [3]. The experiment, which extended over a week, produced only slight decreases in titer. With regard to the very rapid alkaline saponification of the formic acid ester, only traces of the latter can be present in the reaction mixture. After its formation after the first reaction, it must be further saponified at a superior rate under the conditions of our experiment. The rate of the titer decrease is, therefore, essentially indicated by the rate of the saponification of the ortho ether.

In order to test whether the slow saponification of orthoformic acidic ethyl in the soda solution is an aqueous saponification, an acidic saponification, or an alkaline saponification, the ortho ether was introduced into a 0.1N sodium hydroxide solution and its titer decrease was determined with acid and phenolphthalein as the indicator. In this medium, the formic acid ester, which forms slowly according to equation (1), leaves even more rapidly than in the soda solution, and the titer change of the sodium hydroxide indicates the direct conversion of the ortho ether. In the case of the aqueous saponification, the same rate was then to be predicted as in the soda solution--in the case of the acidic saponification, a delayed rate, and in the case of the alkaline saponification, an accelerated rate. The experiment produced constancy of the hydroxide titer for one week. A very slight titer decrease, which could just be observed, is sufficiently explained by the unavoidable absorption of atmospheric carbonic acid by the sodium hydroxide.

Thus, on the one hand, it was made probable that the ortho ether in the soda solution was acidically saponified; on the other hand, it was determined that the orthoformic acidic ethyl is not subject to an alkaline saponification or an aqueous saponification either--in any case, not in the

amount of the otherwise previously found orders of magnitude, an [illegible], which is to be understood in principle and is presupposed by the degree of accuracy of the analysis methods and the duration of the measurements.

If the reaction in the soda solution really is an acidic saponification, a tremendously rapid reaction of the ortho ether was to be expected for a mineral acid solution.

The saponification was therefore investigated in a 0.1-norm hydrochloric acid-acidified solution and the measurement method was set up so that the first stage of the secondary effects, the reaction of the ortho ether to formic acid ester, was revealed. A reaction mixture was prepared that contained 0.1 mol ether and 0.1 mol HCl; samples of this were taken from time to time, and allowed to flow into small flasks, in which there was an excess quantity of 0.1-norm barite, and they were closed with cork plugs with soda lime tubes.

The saponification of the ortho ether had to be at a standstill at the time it was made alkaline; on the other hand, the formic acid formed from it--to the extent that it, in turn, had not been subjected to acidic saponification--had to be subjected to alkaline saponification very rapidly. The titer decrease of the hydroxide present therefore had to correspond to the sum from the formic ester and the formic acid and thus to the quantity of ortho ether consumed in the reaction, after the deduction of the amount for the catalyst acid.

The titer decrease of barite hydroxide always exhibited, both with the sample immediately taken after the preparation of the reaction mixture and also with all later samples, a quantity of consumed ortho ether which was equal to its initial concentration. The experiment was repeated--in order to be very certain--but the first sample taken immediately at the beginning of the reaction always indicated complete conversion of the ortho ether.

The hydrolysis of ortho ether to formic acid ester in mineral acid solution therefore takes place very rapidly. This also had to be demonstrable in a completely different way.

The hydrolysis of the formic acid ester takes place at a moderate, exactly known rate, in mineral acid solution. If ortho ether is reacted in the acidic medium, the case of a two-stage reaction was therefore present, in which the first stage takes place at an outstanding rate, in comparison to the second one; the experiment can be shown by the one-stage rate equation of the slower partial reaction. Therefore, if a measurement method was applied toward the same reaction mixture, which was based on the following of the conversion according to the second stage, the measurement of the produced formic acid, then the result would have to be the already known rate constant of the formic acid ester according to the one-stage monomolecular calculation.

The reaction of the formic acid ester and the orthoformic acid ether in hydrochloric acid solution

The exact measurement of the constants of the acidic saponification of the formic acid ester was done by Palomaa (l. c.) and involved a difficulty which, as in many similar cases, is found in the rapid alkaline saponification of the ester. If one turns namely to the acid titer soda and phenolphthalein determinations, then an increased consumption occurs due to the alkaline saponification of ester still present at the titration endpoint and with the local excess of titer solution at the site of influence.

In such cases, ammonia [4] was frequently selected, which, as a weak base, does not exhibit this disadvantage, but instead makes the titration less exact. Palomaa sought a way out in the middle in that he used the stronger ethylamine.

According to the design of the titration experiment by N. Bjerrum [5], however, the use of weak bases and acids as measurement solutions does not cause any difficulties, and the work is carried out with the best--that is, determined--titration exponents. We therefore used ammonia and 6.35 as the best titration exponents, for which p-nitrophenol is a suitable indicator. The titration error is then 0.03 cm^3 at the beginning and 0.1 cm^3 at the end of the measurement, or 1‰, or 2% of the current ester concentration--this is, it corresponds to the desired accuracy.

The titration of Experiment 1 was carried out in this way. In Experiments 2 to 5, the work was more rapid and simple, in that alizarine was used as an indicator and the titration was pale yellow to purple [6]. The accuracy of this simplified experiment is, as the experiment teaches, also sufficient.

For the rest, the procedure was very similar to that used by Palomaa, only the reaction was undertaken in larger quantities, in that 500 cm^3 reaction mixture were prepared and samples of 50 cm^3 were titrated.

Experimental series 1

Formic acid ethyl ester in hydrochloric acid solution

Experiment 1

$k = 0.00048, S = 0.00034$			
t	$t-x$	k	k
0	0.07970	—	—
15	0.05982	0.0193	0.0193
25	0.04918	0.0192	0.0193
42	0.03518	0.0197	0.0195
60	0.02520	0.0185	0.0192
78	0.01778	0.0193	0.0192
105	0.01072	0.0187	0.0192
(1) Mittel ...		0.0191	
(2) für $S = 1$...		0.102	

Key: 1 Average
2 For

Experiment 2

$$\xi = 0.11255, S = 0.00017$$

t	$\xi - x$	λ	λ
0	0.10230	—	—
S	0.08844	0.0189	0.0182
16	0.07858	0.0180	0.0181
26	0.06362	0.0186	0.0183
38	0.05102	0.0184	0.0183
54	0.03838	0.0178	0.0182
83	0.02304	0.0176	0.0180
<hr/>			
① Mittel... 0.0181			
② für $S = 1...$ 0.183			

Key: 1 Average
2 For

Experiment 3

$$\xi = 0.10835, S = 0.00020$$

t	$\xi - x$	λ	λ
0	0.10042	—	—
7	0.08844	0.0181	0.0181
14	0.07768	0.0186	0.0183
22	0.06882	0.0188	0.0185
32	0.05474	0.0182	0.0184
50	0.03898	0.0185	0.0184
83	0.02242	0.0181	0.0183
134	0.00878	0.0180	0.0182
<hr/>			
① Mittel... 0.0183			
② für $S = 1...$ 0.185			

Key: 1 Average
2 For

Experimental series II

Orthoformic acid ethyl ether in hydrochloric acidic solution

Experiment 4

$\epsilon = 0.12035, S = 0.09788$

t	$\epsilon - x$	k	k
0	0.12035	—	—
8	0.10283	0.0195	0.0195
18 ^{45/60}	0.08860	0.0193	0.0194
27 ^{50/60}	0.07002	0.0194	0.0194
40	0.05548	0.0191	0.0193
55	0.04200	0.0188	0.0191
78	0.02740	0.0186	0.0189
118	0.01260	0.0184	0.0191
(1) Mittel... 0.0191			
(2) k für S = 1... 0.185			

Key: 1 Average
2 For

Experiment 5

$\epsilon = 0.10455, S = 0.08931$

t	$\epsilon - x$	k	k
0	0.09852	—	—
7	0.08423	0.0194	0.0194
15	0.07248	0.0189	0.0191
28	0.05880	0.0190	0.0191
39	0.04630	0.0184	0.0188
56	0.03354	0.0190	0.0189
77	0.02258	0.0188	0.0189
(1) Mittel... 0.0189			
(2) k für S = 1... 0.182			

Key: 1 Average
2 For

In the tables, S signifies the concentration of the catalyst acid (hydrochloric acid), which, like all other concentrations, is indicated in moles per liter; ϵ , the equilibrium concentration of the produced formic acid or the saponifiable fraction of the ester [7]; $\epsilon - x$ the current concentration of the saponifying ester, determined from the current acid titer and χ ; and t, the time in minutes.

The rate constant was calculated according to the formula:

$$k = \frac{1}{t_2 - t_1} \ln \frac{\epsilon - x_1}{\epsilon - x_2}$$

--one time from two directly successive values of t and ϵ , that is, according to the sequence formula [8], and the other time, in the most common manner, according to the step formula, which strips away the errors.

The average value of the constant, related to $S = 1$, of the acidic saponification of the formic acid ester from all three experiments is 0.187 and completely agrees with the one found by Palomaa. The best value, however, should be that of Experiment 1, since it is based on the most accurate titration method (titration with a determined titration exponent). We therefore want to hold on to the value:

$$k = 0.192 \text{ (25°).}$$

Experiments 4 and 5 with the orthoformic acid ethyl ether finally produced a good constancy of k and for the value, related to $S = 1$, of the constant on average $k = 0.1983$ --that is, the same value as for the formic acid ethyl ester.

Thus, it appears to be proved that the orthoformic acid ethyl ether is converted into formic acid ester at an unmeasurably rapid rate in a strongly acidic solution.

Experiment plan for the measurement of the rapid reaction

Since reaction (1) takes place unmeasurably fast in $[H^+] = 0.1$ solutions, but in $[H^+] = 0.1$ or $[H^+] = 10^{-13}$ solutions is practically stationary, it was predictable that it progresses, with an average acidity, at a rate that can be easily measured. It was also obvious that the most suitable acidity should be sought by using various hydrogen ion buffers.

In order to slow the acidic saponification of the ortho ether, it was first undertaken in the reaction mixture (gram formula weights per liter):



that is, with the acidity $[H^+] = 7.2 \cdot 10^{-6}$. The measurement method was the same as the one implemented at the beginning: taking of a sample in excess hydroxide and measurement of the formic ester produced from the ortho ether. The first measurement, undertaken immediately after the start of the reaction, produced a result of 50%. The hydrolysis is therefore also too fast at this acidity for measurement.

Thus, there was a case of hydrogen ion catalysis of a speed so unusual that up to now, it had not yet been observed in acidic saponifications.

The acidic saponification in the acetic acid-acetate solution again justifies the assumption stated in the beginning, wherein the slow reaction observed in the soda solution is an acidic saponification.

The attempt was recently made to measure the reaction in a carbonate solution, wherein to increase the rate, a copious bicarbonate additive was used. In fact, the decrease in soda titer was then a noticeably more rapid decrease but a sign that the ortho ether was actually acidically saponified in the soda solution; however, we soon abandoned those experiments: the reaction was still too slow to give useful results and moreover, the carbonate-bicarbonate buffer with a high bicarbonate concentration cannot withstand an experimental time of many days [9].

Something similar is true for an ammonia-ammonium salt buffer, which permits the reduction of the acidity to $[H^+] = 10^{-[illegible]}$.

Thus, two paths appeared to be still open, wherein by following these paths, a suitable reaction rate was promised: the selection of a buffer with the range around $[H^+] = 10^{-6}$ or one around $[H^+] = 10^{-7}$.

The former path proved less feasible. To be sure, with $[H^+] = 10^{-8}$, abandoning the formal standpoint would have been particularly attractive. As can be seen from the finally determined numerical value of the constant of the ortho ether and the already known one of the acidic and alkaline saponifications of the formic acid ester, the two-stage reaction would really appear here as such. Both partial reactions would have had rates of the same order of magnitude; the first would be the acidic saponification of the ortho ether without acid toning and would have been accelerated by hydrogen ions; the second, the alkaline saponification--the acidic saponification would have been neglected--of the formic acid ester with acid toning and would have been delayed by hydrogen ions. The mathematical expression of the entire process would be a system of simultaneous differential equations of the following form:

$$\left. \begin{aligned} \frac{dx}{dt} &= k_1(a-x) \frac{c+x}{b-y} \\ \frac{dy}{dt} &= k_2(x-y) \frac{b-y}{c+x} \end{aligned} \right\}$$

Without going into the question of the integration of the system or the further possibilities of operating with these equations, one can say that all methods would have made available mathematical expressions of such complexity that their use with regard to the expected accuracy of the analysis results appeared to be of very questionable value. As a result of the simultaneously present buffer salts, a large alkali excess had to be taken, namely, for the determination of the formic acid ester, so that $x - y$ is determined as a small difference, that is, not very accurate. Moreover, especially in the area $[H^+] = 10^{-8}$, there is a lack of a buffer of normal useability.

In this case, like in many similar cases, working toward the simplest and most transparent conditions possible is urgently recommended. Such conditions are given by the acidity $[H^+] = 10^{-7}$ --that is, the measurement of the reaction in the neutrality areas.

Here, a phosphate buffer from primary and secondary phosphate is available. The dissociation constant of the phosphoric acid after the second stage is 1.95×10^{-7} , or with sufficient accuracy, 2×10^{-7} ; the surroundings of a hydrogen ion concentration of numerical value therefore had to be taken into consideration. As a rough calculation showed, the alkaline saponification of the formic acid ester had to take place here very slowly already. Thus it was possible to strive for a very substantial simplification of the conditions. If the reaction of the ortho ether took place so rapidly that the saponification of the formic ester, which influences the acidity, could probably be neglected for the duration of the reaction course which was followed, then an isolation of the reaction of the first step, which is what we are dealing with, and which takes place without acid toning, was attained in a medium of constant acidity--therefore, the simplest time law, the one-stage equation of first order, is applicable to the time process to be measured.

Of the reaction partners, only one was to be analyzed here, the produced formic acid ester, and this could occur only by the alkaline saponification of the latter by an added corresponding excess of hydroxide, wherein the reaction to be measured was appropriately slowed down with an excess, and a subsequent back-titration to secondary phosphate.

In order to find out now whether these desirable experimental conditions could really be implemented, one had to find a clue for the rate at which the ortho ether reacts here, and thus, on the basis of these assumptions and without consideration as to whether they are exactly fulfilled, some orienting preliminary experiments were first carried out with a ratio of the buffer 1:1--that is, with an acidity $[H^+] = 2 \times 10^{-7}$; the possible errors could, in no way, be so large as to be able to at least determine the order of magnitude of the rate of the reaction.

These preliminary experiments showed that the reaction course, in fact, took place in a few hours and produced, as a rounded-off, approximate numerical value, the constant 50,000, relative to $[H^+] = 1$.

The meanings are as follows:

k	constant of the acidic saponification of the ortho ether for $[H^+] = 1$.
k_a	constant of the alkaline saponification of the formic ester for $[H^+] = 1$.
k_2	dissociation constant of the phosphoric acid according to the second stage.
k_3	dissociation constant of the phosphoric acid according to the third stage.
a	starting concentration of the ortho ether.
π	starting concentration of the primary phosphate.
σ	starting concentration of the secondary phosphate.

- h hydrogen ion concentration.
 $w = 10^{-14}$ water constant for 25°.
 x conversion variable of the first reaction.
 y conversion variable of the second reaction.

For k, the orientation value $k = 5 \times 10^4$, for k_a , the value [10] $k_a = 1400$ was used. Because it is simply a matter of the determination of the best experimental conditions, one can be satisfied with approximate numerical values.

For the beginning of the reaction, the following is valid:

$$h = k_1 \frac{\pi}{\sigma} \quad (3)$$

In the course of the reaction, a quantity y of formic acid is formed; it is stronger than the phosphoric acid after the second stage and converts y moles of the secondary phosphate into primary phosphate. Therefore, the following is valid for the current acidity:

$$h = k_1 \frac{\pi + y}{\sigma - y} \quad (4)$$

By setting k as a constant according to (3), we produce an error F. It amounts to the following in percentage:

$$F = \frac{k_1 \frac{\pi + y}{\sigma - y} - k_1 \frac{\pi}{\sigma}}{k_1 \frac{\pi}{\sigma}} \cdot 100 = \frac{y(\pi + \sigma)}{\pi(\sigma - y)} \cdot 100 \quad (5)$$

In order to determine this error in an arbitrary stage of the reaction--that is, for an arbitrary value of z, we need to know the relation between y and x, and because F should be small, then one can be satisfied with an approximate relation. The approximation that we make and that is fulfilled all the better, the smaller F or the more changeable h is, is that we neglect y as small, in comparison to x, π and σ . Then, our simultaneous differential equations are simplified and become:

$$\left. \begin{aligned} \frac{dx}{dt} &= k h (a - x), \\ \frac{dy}{dt} &= k_a \frac{\pi}{h} x, \end{aligned} \right\} \quad (6)$$

where h has the value according to (3).

Then, by division, it follows that:

$$\frac{dy}{dx} = \frac{k_0 w}{k h^2} \cdot \frac{x}{a-x}$$

and integrated:

$$y = \frac{k_0 w}{k h^2} \{ a - x - a \ln(a-x) \} + J.$$

The integration constant J follows from $y = 0$ for $x = 0$. Their use finally produces the following as the sought relation:

$$y = \frac{k_0 w}{k h^2} \left\{ a \ln \frac{a}{a-x} - x \right\}. \quad (7)$$

According to this expression, the y for arbitrary a , x and h can be calculated and by the use of y in (5), the error F , in its dependence on y and the buffer salt quantities π and σ , can be determined.

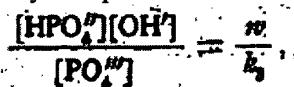
This was carried out for a number of cases, and sufficiently small values of F resulted for a number of them.

The results obtained were evaluated for the experimental conditions to be established, taking into consideration the viewpoints which are to follow.

The only possible type of analysis was already characterized. The main thing was to manage with the lowest possible hydroxide excesses, if the analysis result, as a small difference, was not to be very inaccurate.

Standing in the way of this was the presence of the buffer salt. The lower the quantities of buffer salts to be used, the lower would be the hydroxide quantity. They should not be selected too small, however, since from (5), it is clear that F is all the smaller, the larger the z and π and σ . Between these contrary considerations, therefore, a middle course would have to be sought and found.

The hydroxide excess was to be dimensioned in such a way that the formic ester to be analyzed saponifies quantitatively in a short time. With a small hydroxide excess, it first saponifies in the excess hydroxide and then, when this is consumed, in a mixture of secondary and tertiary phosphate. The reaction time for the ester saponification is sufficiently dimensioned if we calculate it for the alkalinity which prevails at the end of the reaction. This alkalinity follows, in accordance with the hydrolysis equilibrium:



from the following quadratic equation:

$$[\text{OH}'] = \frac{w}{k_s} \cdot \frac{T - [\text{OH}']}{S + [\text{OH}]}$$

or:

$$[\text{OH}]^2 + \left(S + \frac{w}{k_s}\right)[\text{OH}] - \frac{w}{k_s}T = 0, \quad (8)$$

where S and T signify the "analytical concentrations" of the secondary or tertiary phosphate.

If we assume the formic ester to be saponified if it has been reacted to 99%, then the reaction time R is calculated in minutes for the alkalinity $[\text{OH}']$, in accordance with the following equation:

$$k_s[\text{OH}']R = \ln 100. \quad (9)$$

The hydroxide excess was so dimensioned that R is only fractions of a minute. Since the formic ester first saponifies in an essentially alkaline medium, this statement is surely much too generous; however, one is soon convinced that there is not much to spare here.

From these explained viewpoints, a series of experimental conditions were weighed, and the following were selected as the most suitable:

	① Versuchreihe A	② Versuchreihe B
a.....	0.1	0.1
n.....	0.03	0.03
c.....	0.06	0.06
$h(3)$	1×10^{-3}	3×10^{-3}
x.....	0.07	0.08
$x(7)$	0.0014	0.00088
$F(5)$	7.2	3.3
L.....	0.14	0.20
S.....	0.05	0.07
T.....	0.04	0.05
$[\text{OH}'](8)$	0.018	0.013
R(9).....	0.26	0.26

Key: 1 Experimental series A
2 Experimental series B

The error which was calculated from (5) and which flows from the inconstancy of the acidity appears indicated here for that x up to which the reaction was followed by measuring--that is, for the end of the measuring. For the middle and beginning of the

measurement, it is, of course, substantially less, so that the acidity, with sufficient accuracy, should be assumed as constant.

L is the hydroxide quantity used for fixing the reacting system and for saponification of the produced formic ester. It is, like the other concentrations, indicated in moles per liter in the table.

The measurement of the acidic saponification of the ortho ether

The titration was done according to the data from Bjerrum for secondary phosphate--for a titration exponent 9.57, and using a Soerensen standard solution, dyed with the indicator. 13 drops of a 1% alcoholic phenolphthalein solution was used on 100 cm³ of the latter and the titrated-out solution.

With this titration exponent, an acidic saponification of the ortho ether was not to be feared; on the other hand, the use of a strong acid as the standard solution had to be avoided, considering the local acid excess on the influence site, which could lead to an acidic saponification of the ortho ether. The latter takes place without acid toning, that is, would be, in fact, without disadvantageous effect, but leads to the formic ester, the latter of which is subjected to an alkaline saponification in the solution to be titrated and would bring about an erroneous reduced consumption of titration acid. For this reason, 0.1-norm acetic acid was used as the standard solution, which was without importance for the accuracy of the titration, since the dissociation constant of the acetic acid is substantially greater than k_2 of the phosphoric acid.

The execution of the experiments took place in the following manner:

As buffer salts, the Kahlbaum preparations KH_2PO_4 and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ "according to Soerensen" were used. The weighed quantities were dissolved in a volumetric flask to 500 cm³ in boiled water and the ortho ether, weighed in by means of a Rey pipette, was added to the reaction flask, filled to the mark; it was quickly brought to 25° and the reaction flask was suspended in the thermostat.

The reaction flask was provided with a lifting apparatus which could be closed, which permitted taking samples with the smallest possible evaporation losses. They were captured in a volumetric flask to 50 cm³ and from this, brought to a beaker (time reading), in which the required quantity of hydroxide had already been added from an automatic pipette. After waiting for some time (1/4 minute, see above), the back-titration with acetic acid took place.

The calculation was carried out according to the following formula:

$$k = \frac{1}{t_2 - t_1} \ln \frac{a - x_1}{a - x_2} \quad (10)$$

The method, as it was described, did not allow us to expect any special accuracy, since despite all limitation, one had to work with sizeable hydroxide excesses; the current

concentration $a - x$, therefore, came out as a small difference. In addition, there are the unavoidable mistakes, as a result of the effect of atmospheric carbonic acid, which is always connected with investigations in which one must deal with strongly alkaline solutions for some time.

Finally, another error source was taken into consideration, whose influence could not yet be extensively eliminated, and which suppressed the degree of accuracy by another stage. This was the evaporation of the formic acid ester, which, by itself, boils at 54° and has a high partial vapor pressure in the 25° reacting mixture.

This fact of the accurate measurement of the acidic and alkaline saponification of that ester is not very restricting. With these rapid reactions, the concentration of the volatile reaction partner decreases rapidly with time, with the formation of nonvolatile reaction products, which are measured. Here, however, the concentration of the volatile substance increases with time and has the greatest values toward the end, that is, in the second unequally longer parts of the reaction, and the volatile substance being formed is used for the measurement of the reaction progress.

The mode of sampling mentioned above could also only reduce but not eliminate this evil, since with the length of the reaction and the gradual emptying of the reaction flask, the air space in the latter and thus the evaporation are greater and greater.

The loss as a result of the evaporation can also be seen from the experimental tables for the values indicated there for the time infinity. The way out, which is often selected in such cases, namely, to determine the current concentrations not from the starting values, but rather from the end value, was not feasible here, because, in fact, the concentration of the reacting substance was not reduced by the evaporation, but rather the concentration of the volatile reaction product to be measured.

In the following tables, a signifies the weighed quantity of ortho ether, which was the basis of the calculation; X_{∞} the quantity of formic ester found by analysis at the end of the reaction. Because a reverse reaction is certainly not present, $X_{\infty} = a$ should have been expected. As a result of the evaporation, $X_{\infty} < a$ was found. The described phenomenon is manifested, above all, in a strong decrease of the constant in the last fourth of the reaction. In Experimental Series B, whose reactions were followed longer, the gradient is shown more clearly than in Experimental Series A. The constant values found too small as a result of the evaporation were placed in parentheses in the tables and were omitted in the calculation of the average. In the following, we have the measurements.

Experimental Series A

$$k = 1 \times 10^{-1}$$

Experiment 6

$$a = 0.10949, x_{\infty} = 0.10388$$

t	$a-x$	kh	kh
0	0.09859	—	—
29	0.08264	0.0071	0.0071
57	0.06631	0.0069	0.0069
94	0.05195	0.0066	0.0069
153	0.03497	0.0067	0.0068

$$kh = 0.00670$$

Experiment 7

$$a = 0.11700, x_{\infty} = 0.10576$$

t	$a-x$	kh	kh
0	0.10550	—	—
23	0.08958	0.0071	0.0071
47	0.07684	0.0068	0.0067
82	0.06094	0.0065	0.0067
125	0.04580	0.0066	0.0066
185	(0.03210)	0.0059	(0.0064)

$$kh = 0.00664$$

Experiment 8

$$a = 0.11340, x_{\infty} = 0.10590$$

t	$a-x$	kh	kh
0	0.0952	—	—
21	0.0835	0.0062	0.0062
46	0.0703	0.0069	0.0069
77	0.0564	0.0071	0.0068
118	0.0423	0.0070	0.0069

$$kh = 0.00683$$

Experiment 9

$$a = 0.11203, x_{\infty} = 0.10448$$

t	$a-x$	kh	kh
0	0.10543	—	—
19	0.09369	0.0062	0.0062
46	0.07637	0.0075	0.0070
77	0.06255	0.0064	0.0068
115	0.04863	0.0066	0.0067
169	0.03433	0.0064	0.0068

$$kh = 0.00669$$

Experimental Series B

$$h = 2 \times 10^{-1}$$

Experiment 10

$$a = 0.00733, \quad x_{\infty} = 0.08986$$

t	$a-x$	kh	kh
0	0.08405	—	—
15	0.08807	0.0141	0.0141
53	0.03987	0.0141	0.0141
81	0.02885	0.0144	0.0148
117	(0.01847)	(0.0102)	(0.0129)
166	(0.01259)	(0.0078)	(0.0114)
		$kh = 0.01415$	

Experiment 11

$$a = 0.10527, \quad x_{\infty} = 0.09621$$

t	$a-x$	kh	kh
0	0.08927	—	—
9	0.07903	0.0135	0.0135
20	0.06705	0.0149	0.0143
34	0.05535	0.0137	0.0141
69	0.03541	0.0127	0.0134
100	(0.02451)	(0.0119)	(0.0129)
136	(0.01709)	(0.0120)	(0.0120)
		$kh = 0.01373$	

The first series kh was always calculated by interval integration; the second, by integration from the very beginning. The average values of kh were calculated from all combinations of all measurement results not placed in parentheses.

Better constancy of kh within the individual experiments could not be expected according to the cited error sources.

The values of the experimental series A give, in turn, the following as the average:

$$kh = 0.00674 \quad (h = 1 \times 10^{-7})$$

and the two of the experimental series B:

$$kh = 0.01394 \quad (h = 2 \times 10^{-7})$$

Therefore, they are also like the acidity in the ratio 1:2, with a deviation of only approximately 3%.

Thus, it appears to be proved that the hydrolysis of the orthoformic acid ethyl ether to formic acid ethyl ester can be calculated as a one-stage reaction, whose rate is proportional to the concentration of the ortho ether and hydrogen ion.

If one relates the rate to the concentration unit of the ortho ether and hydrogen ion, one obtains 6.85×10^4 , or rounded off:

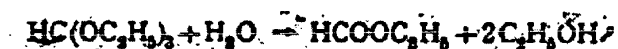
$$k = 70,000 (25^\circ)$$

From this, a midpoint of $[H^+ = 0.1]$ minutes follows for 1×10^{-4} or--for the result as 99%--a reaction time of $6 \times 10^{-[illegible]}$ minutes, in agreement with the results of the measurements in 0.1-norm HCl solution.

The results of the preliminary experiments also agree with the numerical value of the constant. On one hand, 1 minute is calculated from it, namely for the mid-point in the acetic acid experiment ($h = 7 \times 10^{-6}$); on the other hand, for the result as only 10%, a reaction time of 20 days for the carbonate-bicarbonate experiment ($h = 6 \times 10^{-11}$) and of 10,000 days for the hydrolysis by 0.1N NaOH ($h = 10^{-13}$).

The chemical nature of the ethyl orthoformate

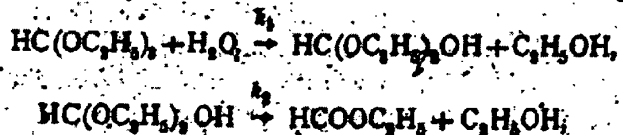
According to the result of our measurements, the orthoformic acid ether thus reacts in the sense of the following equation:



at a rate h , which is proportional to the hydrogen ion concentration. For $[H^+] = 1$, k has the tremendous value of 70,000.

The question of whether this rapid acidic hydrolysis takes place directly, at one go, or via intermediate stages, remains unanswered. Both assumptions are compatible with the results of the measurements. The "chemical feeling" is an argument for the stagewise course. The tendency to assume stagewise reactions in the present case and in similar cases corresponds to our current molecular-kinetic views, based on probability-theoretical views and supported by general experience.

If we follow this tendency, we would have assumed at least two stagewise reactions:

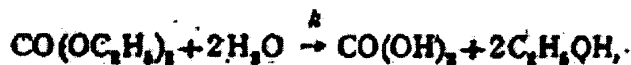


where between k_1 and k_2 , equations would have to be valid, which have such a nature that in measurements, the stagewise sequence with the constants k_1 and k_2 behaves exactly as the direct reaction with the constant k . There are two relations which satisfy this condition,

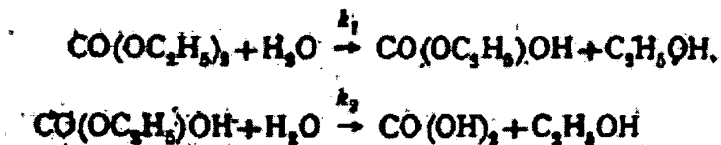
1st case. The constant k_1 is very large in comparison to k_2 . The orthoformic acid ester is converted into the intermediate substance $\text{HC}(\text{OC}_2\text{H}_5)_2\text{OH}$ relatively rapidly and what is measured is the conversion of the latter into formic ester. The measured constant k is $k = k_2$. The circumstance that the intermediate substance could neither be isolated nor proved up to now speaks against this hypothesis. Since neither formic ester nor its saponification products are formed in the alkaline-rendered medium, k_2 can be only very small in this medium. By dissolving the ortho ether in dilute acid and the immediate alkalization of the solution, the ortho ether would have been converted almost completely into the intermediate product and it should have been possible to detect the latter then and, for example, to isolate it by vacuum distillation. That the preparative art has not yet succeeded in doing this speaks against the assumption $k_1 \ll k_2$.

2nd case. The constant k_1 is very small in comparison to k_2 . The ortho ether forms the intermediate product $\text{HC}(\text{OC}_2\text{H}_5)_2\text{OH}$ relatively slowly; it is reacted to formic ester, in turn, relatively fast. The measured constant k is $k = k_1$. That the intermediate substance has not yet been detected, not to speak of being isolated, speaks in favor of the assumption $k_1 \ll k_2$,

However, direct observations made with another substance which has hydroxyl and alkoxyl bonded to the same carbon speak for $k_1 \ll k_2$. We are referring to the saponification of the carbonic acid [11]. This reaction also takes place like a one-stage reaction, according to the measurements:



which, just like the hydrolysis of the formic acid ortho ether, can be thought as broken down into the stage sequence.

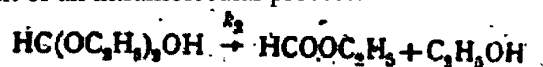


Here, however, we have the possibility of exposing the second of the two stagewise reactions in that it is possible to prepare the intermediate substance in the form of a sodium salt and to investigate it directly with regard to its reactivity. If one brings this sodium salt into aqueous solution, then the experiment teaches that it reacts with all ratios--that is, with any acidity taken into consideration--almost instantaneously to form carbonic acid and alcohol.

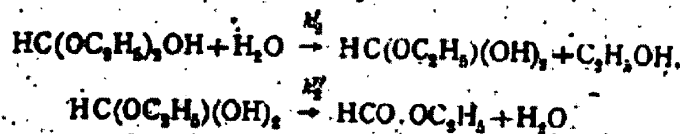
If we accordingly break down the measurable reaction of the saponification of the carbonic acid ester into a stagewise sequence, then as regards the constants of the stage sequence, $k_1 \ll k_2$ and $k = k_1$ are necessarily linked to this breakdown, as additional conditions.

The conditions with the carbonic acid ester and the additional circumstance that very generally, the monoalkyl and monoaryl derivatives of the geminal glycols "are mostly difficult to understand" [12] are an argument for the fact that we have also assumed that $k_1 \ll k_3$ and $k = k_1$ for the stage sequence of the ortho formic acid ether hydrolysis as probable.*

Analogous with the carbonic acid ester, the rapid reaction, according to the second stage, can also be either the result of an intramolecular process:



or that of another stagewise sequence:



with our ortho ether also, wherein it was not possible to reach a decision.

*[Molecular-kinetically, one has thus said the following. It is the stagewise reaction of a substance with two identical and identically bonded reactive groups X. Such a substance has the structural formula XAAX, It reacts according to the following stagewise scheme:



If one designates with u the constant of the group rate of the substance XAAX--that is, the speed at which a certain group X of this substance reacts, then the rate k_1 at which one or the other group reacts in XAAX is $k_1 = 2u$. With regard then to the rate k_2 after the second stage, then one should distinguish here among three cases:

1. The reaction of the group X takes place independently--that is, (see R. Wegscheider Monatshefte für chemie, 9 (1908), 91 and 36 (1915), 471), uninfluenced whether the second group X is still present or is already replaced by X. Then, $k_2 = u$.

This case is, among other things, realized in the acidic saponification and esterification of the normal oxalic acid homologs and tartaric acid and in the acidic and alkaline saponification of the esters of ethylene glycols. In the electrolytic dissociation of divalent symmetrical acids and bases, it is present, if the ratio $\delta_1:\delta_2$ of the constants of the stagewise electrolytic dissociation is 4, which is approximately true with phenolphthalein and with crystal violet, since there is a connection between $\delta_1:\delta_2$ and the ratios of the kinetic constants of the stagewise sequences of the electrolytic dissociation.

2. The reactivity of the group X is a dependent one in the manner that X reacts more slowly if the other X has already reacted--that is, is replaced by Z. Then, $k_2 < u$. This case appears to be the rule. It is, for example, realized in the alkaline esterification of the esters of the normal oxalic acid homologs and tartaric acid. It is also realized in the stagewise electrolytic dissociation of the symmetrical acids and bases, in that $\delta_1:\delta_2$ is large as a rule and very frequently, very much larger than 4. (see E. Q. Adams, Journ. Am. Chem. Soc., 38(1915), 1503).

3. The reaction of the group X is an independent one in the manner that X reacts more rapidly if the other X has already reacted. Then, $k_2 > u$. This case is realized in the saponification of the carbonic acid ester. It appears to be realized, perhaps very generally, in the saponification of the ethers and esters of geminal glycols.]

Another question to be discussed on the basis of our reaction-kinetic finding is that of the characterization of the chemical nature of ethyl orthoformate. In this regard, in any case, one can say that the latter has to be eliminated from the class of esters and classified as an ether.

If R designates an alkyl and A, an acyl, then it is possible to establish three types of substances with an ethereal bonded oxygen atom with regard to the process of the hydrolysis and the all the rest of the chemical characteristics:

Type I (ethers): ROR'

Type II (esters): AOR'

Type III (anhydrides): AOA'

This separation is not to be understood as a fundamental one but rather probably only as a gradual one, since, as P. E. Verkade [13] has shown, there is extensive agreement between the carbonic acid, on the one hand, and alcohol, on the other hand, and with regard to the chemical behavior of the two substance classes--if one disregards the specific reactions of carbonic acids caused by the carbonyl group--there is no basic difference.

If, on the one hand, an analogy exists between acyl and alkyl, then there is, on the other hand, such an analogy between alkyl and hydrogen. The view of the hydrogen atom as the simplest alkyl of saturated hydrocarbons goes back to J. H. van't Hoff [14] and was recently explained convincingly, namely, by K. Kubierschky [15]. Our overview therefore includes the free carboxylic acids and limiting cases of the esters and alcohols and water, as limiting cases of ethers. The important reaction of the saponification or hydrolysis proves to be then a case of "ester interchange," wherein one understands the phenomenon that the substances with an ether oxygen in reaction with other substances with ether oxygen are able to exchange their acyls and alkyls.

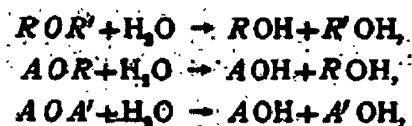
If one assumes multivalent alcohols and carboxylic acids as well as zwitter structures and the oxycarboxylic acids, then these substances are able to form internal ethers, esters, and anhydrides, in addition to the "external" ones. The carbonyl compounds, for example, are then to be understood as internal ethers of geminal glycols. Therefore, all organic compounds with an oxygen atom whose two valences are bonded to C or H fall into our overview.

Other organic compounds can be conceived, once again proceeding from our three types, derived in such a manner that R, A, RO, AO, or O are, stepwise, replaced by other analogous elements or element groups, wherein one arrives at compounds which, with regard to behavior and synthesis, exhibit a closer or more distant analogy with ethers, esters, and anhydrides. In this

way, one arrives at a nomenclature of the organic compounds whose original type is designated as the most general of our three types, the ester type.*

Therefore, if clear transitions and continuities exist, then it is nevertheless recommendable, in the interest of the classification and the categorizing of individual substances into groups belonging together, to first stress what differentiates and separates. The showing of continuities and the search for laws for their gradation are tasks of later development.

The process of hydrolysis or saponification belongs among the reactions of our three substance types, which are also investigated quantitatively and therefore are known with the most accuracy:



the reactions, in a correspondingly strong dilution, take place more or less completely.

The principle of chemical kinetics regarding all possible reactions as also actually taking place, which comes from the general striving toward as uniform as possible an explanation of all natural events, leads us to assume the general time law of a secondary effect for the process of hydrolysis with unchangeable water concentration:

$$-\frac{dV}{dt} = k_a[OH']V + k_s[H']V + k_w V, \quad (11)$$

where V signifies the concentration of the hydrolyzing substance. The three rate constants k_a , k_s , k_w should be designated as the constants of the alkaline saponification, the acidic saponification, and the aqueous saponification.

The concentrations $[OH']$ and $[H']$ are not independent of one another, but rather linked by the following relationship:

$$[H'] [OH'] = w, \quad (12)$$

wherein it should be noted that the reaction leading to this equilibrium condition is established, according to experience, at an outstanding rate, so that the equation (12) is always fulfilled.

From (11) and (12), it can readily be seen that with a certain acidity, the rate of saponification $-dV/dt$ must be a minimum. We experience the minimum condition if after inserting $[OH']$ from (12) into (11), we differentiate the latter equation according to $[H']$ and set the derivation equal to zero, wherein we receive the following:

* It would be very appealing to go into more detail regarding the "ester nomenclature" of the organic substances. I will postpone this until more experimental material, above all, rate measurements are available. The "reactivity" of the substances, the "mobility" of the atom and groups find their exact expression in the rate constants, wherein one has to consider that, as is known, the occurrence or nonoccurrence of a conceivable reaction in organic chemistry is far more frequently based on kinetics than energy, from which the importance of chemical kinetics for organic chemistry may be deduced. (A. S.)

$$[H] = \sqrt{\frac{k_a}{k_s}} \quad (13)$$

We can also write the condition (13) in the following form:

$$\frac{[H]}{[OH]} = \frac{k_a}{k_s} \quad (14)$$

which says that the rate of saponification is a minimum, if $[H\bullet]$ behaves relative to $[OH^-]$ like the constant of the alkaline saponification to the constant of the acidic saponification.

If we conceive of the saponification taking place with a constant acidity, perhaps regulated by a suitable buffer, then its minimum rate is given by the following equation:

$$\frac{-dV}{dt} = 2k_m V + k_w V_A \quad (15)$$

where k_m has the following meaning:

$$[OH^-]k_a = [H^+]k_s = k_m \quad (16)$$

On the other hand, there are two maximum values of rates of saponification, whose conditions can be approached by using solutions as alkaline as possible, or as acidic as possible; in this undertaking, however, one encounters limits, theoretically and practically.

The task of the kinetics is to determine all three saponification constants numerically, at least according to the order of magnitude. Relatively high values of one or the other of the constants can be easily measured, or if the pertinent reaction is immeasurably fast, can be easily determined. The case is different with relatively small values.

If a small constant of the water saponification is to be measured, then one will bring about the condition of the minimum rate. Then, k_w will still have to be measured, if it is of the same order of magnitude as $2k_m$ [see equation (15)]. If $k_w \ll 2k_m$, then there is no prospect of being able to determine its value.

For the purpose of measuring a relatively small k_a or k_s , one will approximate the conditions of the maximum rates. The case that one cannot measure, for example, k_s in a strongly acidic solution, because even under this condition, $k_s [H\bullet]$ is small, in comparison to $k_a [OH^-]$, is hardly expected according to previous experiences which have been gained with regard to the order of magnitude of the constants. According to these experiences, the range of the saponification constants, although large, is substantially smaller than that of the realizable acidities of around 14 powers of ten. In the most extreme case, therefore, one will be able to determine a halting of the saponification and thus the inability to measure k_s as a result of its smallness.

On the other hand, it may happen that one cannot get any idea regarding the order of magnitude of k_s because even in very acidic solution, is small in comparison to $k_s [H\bullet]$. Then,

occasionally, by adding an inert solvent, it is possible to shift the ratio $k_s [H^+]:k_w$ enough, in favor of $k_s [H^+]$, so as to at least be able to establish the fact of the existence of an acidic saponification.

If we now survey the saponification of our three substance types with ether oxygen atoms, with regard to the absolute and relative values of k_a , k_s and k_w , then one can state the following on the basis of previous observations and measurements.

Carboxylic acid esters. The constant of the alkaline saponification is very large and very different with the individual esters. For example, for the first methyl of the oxalic acid ester, it is of the order of magnitude $[16] 10^6$; for a large number of other methyl esters, the order of magnitude 1 and below.

The constant of the acidic saponification is small; with the various esters, not very different, of the approximate order of magnitude $10^{-[illegible]}$ and below.

The saponification rate minimum is, accordingly, in the vicinity of the neutral point, but always on the acidic side of the sample, for example, for ethyl acetate with $[H^+] = 3 \times 10^{-6}$.

An aqueous saponification can generally not be determined--which says that a possible k_w is, under all conditions, small in comparison to $k_a[OH^-]$ or $k_s[H^+]$. If measurements are present in the saponification minimum [17], they are an argument for a vanishingly small k_w , even in comparison to $2 k_m$ [equation (15)]. It would be desirable to increase these measurements and in particular to extend them to esters with extreme saponification rates.

Alkaline, in addition to acidic saponification, with nondetectable aqueous saponification and $k_a > k_s$ require, with the carboxylic acid esters, a sharply pronounced saponification minimum in the area of the weakly acidic reaction, as can be seen from curve II of the figure (abscissa acidity, ordinate reaction rate for $V = 1$, both in a logarithmic count) on the ethyl acetate as an example.

The relations between the three constants, explained here, are valid, as a rule, only for the carboxylic acid esters. With sulfonic acid esters and mineral acid esters, the conditions are substantially different [18].

However, with the carboxylic acid esters also, there are remarkable deviations from the rule. Thus, H. Johansson and H. Sebellus [19] have been able to detect a measurable aqueous saponification, in addition to an immeasurably rapid alkaline saponification* and a measurable acidic saponification during the hydrolysis of the glycolide to glycolglycolic acid and the lactide

* In the meantime, we were able to measure this rapid reaction so that now an ester is present in the lactide, of which all three constants k_a , k_s and k_w are known according to the numerical value. We will soon report on our measurements.

to lactolactic acid. The case of a carboxylic acid ester saponification, therefore, is present here, in which k_w can no longer be neglected, in comparison to $[H^+] k_s$.

As regards lactones, γ -lactones behave normally--that is, like the majority of the other carboxylic acid esters. As concerns β -lactones, on the other hand, the same researchers [20] were able to show particularly extreme deviations from normal behavior, if the hydrolysis of the β -lactones is not catalyzed by the hydrogen ion (or is catalyzed only a little).

With regard to the valid relation $k_w \ll [H^+] k_s$, the β -lactones already bring to mind the acid anhydrides.

Carboxylic acid anhydrides. The saponification or hydration of carboxylic acid anhydrides [21] is characterized by a high value of the constant of the water saponification. For example, $k_w = 0.17$ for acetic anhydride at 25° , corresponding to a mid-point of around 4 min. In comparison to this amount, $[H^+] k_s$ is difficult to validate, and the claim by A. C. D. Rivett and N. V. Sidgwick [22] that the hydrogen ion does not accelerate the hydration of acid anhydrides is easily understandable. On the other hand, K. J. P. Orton and M. Jones [23] are able to state that this hydrolysis is also accelerated by the hydrogen ion, although not as obviously as the ester saponification. The two researchers have also shown that the acids are, namely, very effective catalysts in water-poor media. In addition to the water saponification, therefore, the acidic saponification of the anhydrides is certain.

The acceleration of the hydration of anhydrides by acids (hydrochloric acid, sulfuric acid), moreover, is very clearly obvious also from older observations of a more qualitative nature [24].

The hydroxyl ion is an extraordinarily effective catalyst for the hydration reaction. The constant of the alkali saponification could not yet be determined up to now [25]. The difficulties lie less in the high value of k_a than in the magnitude of k_w , i.e., are of a similar type as those which oppose the determination of k_s . Since the saponification in a medium-strong acidic solution is a purely aqueous saponification, $[OH^-] k_a$ must be small in comparison to k_w in these solutions. Therefore it would be easy to reduce $[H^+]$ in such a way that $[OH^-] k_a$ is large in comparison to k_w ; then $[OH^-] k_a + k_w$ is all the larger, however, because k_w has, in fact, a high value and thus the reaction arrives at the limit of measurability. One has to reckon with these difficulties, therefore, in the measurement of k_a . In any case, it is already possible to say today that the k_a of slowly alkaline-saponifying anhydrides is approximately as large as the k_a of rapidly alkaline-saponifying esters.* Therefore, the reactivity of an acyl A with regard to the alkaline

* I hope to be able to report soon on the alkaline saponification of anhydrides, at least as concerns the order of magnitude of k_a . (A. S.).

saponification in the anhydride AOA' is generally larger than in the ester AOR, so that anhydrides undergo alkaline saponification more rapidly, on average, than esters.

According to what has been said, the saponification curve of carboxylic acid anhydrides has approximately the course of curve III of our figure. Since the ratio $k_a:k_s$ has a greater value than with the esters, the saponification minimum is shifted more toward the acidic side and as a result of the relation $k_w \ll 2k_m$, moreover, completely leveled.

Ethers. In comparison to esters and even more, in comparison to carboxylic acid anhydrides, ethers are very frequently, but not always, characterized by great reactivity. This low reaction capacity is manifested also in their behavior in the hydration or saponification process. Many ethers react with water, only very slowly, to form alcohol and this slow reaction is very probably an acidic saponification.

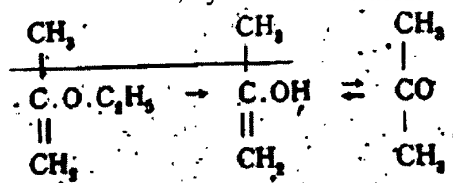
The oldest pertinent observations on ethyl ether are owed to A. Lieben [26]. Pure ether exhibits an iodoform reaction as a result of alcohol formation, in the presence of water, after a few months, more rapidly at 100° in a sealing tube. The circumstance that basic bodies, such as lime and caustic potash, do not attack the ether according to Lieben, whereas acids and salts change it, is an argument, with some probability, that the reaction with water is not a purely aqueous saponification either, but rather an acidic saponification, caused by the hydrogen ions of the water. It is therefore always $[H \cdot]k_s > k_w$.

That the hydrolysis of ethers is an acidic saponification follows from numerous observations of rapidly hydrolyzing ethers and from some measurements. The value of the constant k_s is very dependent on the nature of the alkyl. According to Eitekkoff [27], the ethers of tertiary alcohols are saponified more rapidly than the ethers of secondary alcohols; the latter again more rapidly than the ethers of primary alcohols; the ethers of unsaturated alcohols saponify more rapidly than the ethers of saturated alcohols.

Enol ethers [28] hydrolyze particularly rapidly under the influence of acids, or the hydrogen ion. Thus, vinyl ethyl ether is smoothly split into alcohol and aldehyde, according to Wislicenus [29], by allowing it to drip into dilute sulfuric acid:



According to A. Faworsky [30], isopropenyl ethyl ether is completely broken down into alcohol and acetone, rapidly and when cold, by 1% sulfuric acid:



Just as the ethers of tertiary alcohols hydrolyze more rapidly than the ethers of secondary alcohols, the ethers of tertiary enols also appear to react more rapidly than the ethers of enols whose hydroxyl is secondarily bonded.

The greater hydrolysis rate of enol ethers, in comparison to the lower rate of ethers of unsaturated alcohols, corresponds to the much greater influence of the α -substitution, in comparison to the β -substitution.

In contrast to the rapidly hydrolyzing ethers of tertiary enols, phenol ethers are characterized by a great stability, a sign that not only the type of bonding of the alcohol group, but rather the entire core structure of the alkyl is decisive for the reaction rate.

Furthermore, aldehyde and ketone acetals have an ether nature.* They are rapidly hydrolyzed in the presence of acids to alcohol and aldehyde, or ketone [31]. Here too, acetals of ketones appear to react more easily than those of aldehydes [32].

Following acetals, polysaccharides and glycosides should be noted. Their hydrolysis, like the much investigated cane sugar inversion, or the splitting of salicin into dextrose and saligenin [33], are acidic saponifications, in that the hydrolysis rate is proportional to the hydrogen ion concentration.

The ether character in carboxylic acid ethers, which have three alkoxyl groups bonded to the same carbon atom, appears potentiated to a certain extent. Acidic saponification takes place here, as we were able to show for one case, at a great rate in a neutral solution also; indeed, this was even possible in a weakly alkaline solution, at a noticeable rate.

The designation of alkylated orthocarboxylic acids as esters is thus not justified. The hypothetical parent substances also bear their name incorrectly; they should be properly designated as geminal glycerols; the first member $\text{HC}(\text{OH})_3$ should therefore be called a methenyl glycerol [34].

If one places the value 70,000 for methenyl glycerol ethyl ether, 0.01 for the sugar cane inversion [35], and the surely very small value of the acidic ethyl ether hydrolysis, which has not yet been quantitatively measured, in parallel, one obtains an idea of the range within which the k_s of the ether saponification can fluctuate.

This range surely does not stand, to an extent, according to the range of k_a in the ester saponification and is supposedly just as comprehensive as the range of k_a of the anhydride saponification.

Reactive ethers are also characterized by a large k_s , like the most reactive anhydrides are by a large k_a . Esters hold the middle; their reactive representatives have high values of k_s and k_a ,

* At present, we are busy with the measurement of the hydrolysis of acetals and acyl derivatives of geminal glycols, the latter having a natural ester nature. (A. S.)

which, however, supposedly remain behind, measured on the values of k_s , or k_a of reactive ethers, or anhydrides.

The general reactivity of ethers, esters, and anhydrides runs symbatic to the saponification rate. The rapidly saponifying representatives of these substance classes are therefore also the most effective alkylation or acylation agents. They are used in the synthesis. The slowly saponifying agents are, on the other hand, of practical importance as inert solvents.

According to the numerical values of the saponifying constants, the ethers of saturated, primary alcohols, above all, are taken into consideration for this purpose.

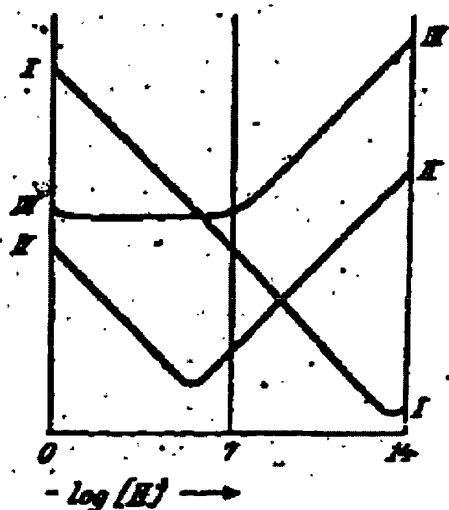
As concerns k_a and k_w of the ether saponification, there are no signs for a noticeable water saponification, to the extent that measurements are available. Similarly as with the esters, therefore, k_w should probably be small also, in comparison to $[H^+]k_s$.

On the other hand, signs of an alkaline saponification are present at times, even though the areas where ethers predominantly undergo an alkaline saponification hardly fall any longer into the range of aqueous solutions.

Thus, the phenol ethers are split with a longer heating with alcoholic alkali or by the alkali melt [36]. Ethers of multivalent phenols are partially or stagewise saponified, just like the esters of multivalent carboxylic acids [37].

In any case, the k_a is very small in comparison to the k_s with the typical ethers, so that the saponification minimum should lie in strongly alkaline areas and, from time to time, should not even be realizable. From constancy reasons, however, one should be able to infer a saponification minimum.

Curve I of the figure shows the course of the saponification curve of the ethers, as we, to some extent, are justified in assuming it, on the basis of our previous experience, as typical for this substance class.



If we consequently arrange the three substance types with the ether oxygen atom into the following series:

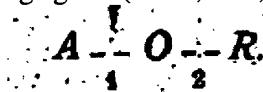
ethers, esters, anhydrides,

then the numerical values of k_w and the ratio $k_a:k_s$ increase in the same sequence, whereas the saponification minimum is shifted from the area of the strongly alkaline reaction into the area of the acidic reaction and at the same time, flattens out more and more.

It was already stressed that all gradations are able to appear here. Thus, the phenol ethers impart the transition from ether to the slowly saponifying esters; the lactides and β -lactones, the transition from esters to carboxylic acid anhydrides. It will be possible to frequently find such transitions with a further study of the saponification phenomenon.

Of the three substance types, esters have been investigated the best and accordingly the theory of ester saponification* has flourished the most. Every new standpoint will be able to cast new light also on this much discussed problem. The question is whether this does not apply also to the standpoint of the analogy of the three substance types with the ether oxygen atom, assumed by Verkade and, in the present case, also by us.

As van't Hoff has already explained [38], the ester AOR has two places in the molecule on which the attack of the saponifying agents (water, acid, base) can take place:



He suspects that during the saponification by alkali, the attack takes place at site 2 and during the saponification by acids, at site 1, and supports his suspicion on the status of investigations at the time, wherein the rate during the alkaline saponification was to be determined primarily from the nature of the alkyl and, during the acidic saponification, on the nature of the acyl.

The material available to van't Hoff is quite insufficient. One needs only to look at the values of k_a for the methyl ester of formic acid, acetic acid, benzoic acid, oxaminic acid**, oxalic acid, malonic acid, sebacic acid, etc., in order to immediately see how enormously great is the influence of the acyl during the saponification with bases. Thus, van't Hoff's suspicion collapses.

From the fact wherein k_a is very large, in comparison to k_s with acid anhydrides, which have only site 1, and very small at that, in comparison to the ethers which have only site 2, one

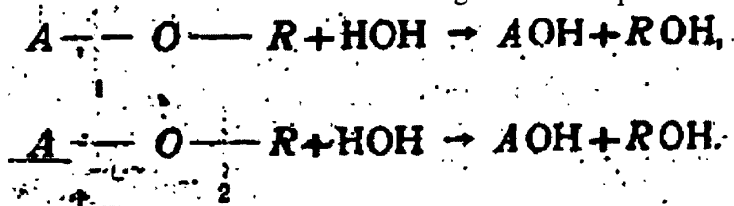
* References to comprehensive explanation of these theories may be found in H. Johansson and H. Sebelius, Ber. Chem. Ges., 52 (1919), 747, Footnote 3.

** The publication of an investigation on the oxaminic acid ester saponification is taking place approximately simultaneously. (A. S.)

would rather conclude that during the ester saponification by alkali, the attack takes place at site 1 and, by acids, at site 2. Therefore, exactly the opposite of the van't Hoff hypothesis.

One would proceed more correctly, however, if the view is again adopted, wherein every possible reaction actually takes place. Then it must be assumed that with all three types of ester saponification (alkaline, acidic, and aqueous saponification), the attack takes place at both sites 1 and 2, since anhydrides that have only site 1 de facto follow all three saponification routes, and ethers that have only site 2 follow at least basically all three saponification routes.

For the esters--and analogous for the "mixed ethers" and "mixed anhydrides"*, reflections which one can generally make and, in a similar manner, has also repeatedly made for substances with two reactive groups are then valid. The saponification of the ester AOR takes place according to the two secondary reactions or--because the latter are identical and different only with respect to their "reaction mechanism"--according to the two "quasissecondary reactions":**



If x_1 signifies the conversion and k_a' , k_s' , k_w' , the three constants of the first reaction; x_2 , k_a'' , k_s'' , k_w'' , the corresponding variables of the second reaction, then the following is valid for the only measurable summation rate:

$$\begin{aligned} \frac{dx}{dt} &= \frac{d(x_1 + x_2)}{dt} = \\ &= (k_a' + k_a'')[\text{OH}'](a - x) + (k_s' + k_s'')[\text{H}'](a - x) + (k_w' + k_w'')(a - x), \quad (17) \end{aligned}$$

if a is the starting concentration of the ester.

A comparison with equation (11) gives the following relations for the constants k_a , k_s , k_w of the saponification of the ester AOR:

$$\left. \begin{array}{l} k_a = k_a' + k_a'' \\ k_s = k_s' + k_s'' \\ k_w = k_w' + k_w'' \end{array} \right\} \quad (18)$$

* This mode of designation appears to us not only shorter, but rather also more correct than the usual one: "mixed ethers" and "mixed anhydrides."

** If the inequality of the two halves of the molecule is not attributable, like here, to the two ligands, but rather to the nonsymmetry of the nucleus, that is, if the substance with the unequal halves is of the formula X-AB-X, then actual secondary reactions take place with secondary effects.

If the two reactive groups bonded to the ether oxygen atom are identical, then a "pure ether" ROR or a "pure anhydride" AOA is present, and $k_a' = k_a'$, etc., is necessary and accordingly:

$$\begin{aligned} k_a &= 2k_a' = 2k_a'', \\ k_s &= 2k_s' = 2k_s'', \\ k_w &= 2k_w' = 2k_w''. \end{aligned}$$

Then $0.5 k_a$, $0.5 k_s$, $0.5 k_w$ signify the rates at which a certain group from the pure ether or the pure anhydride saponifies, or the "group rate." They are, of course, half as great as the rates k_a , k_s , k_w , at which one or the other of the identical groups react.

With pure ethers and pure anhydrides, the group constants k_a , k_s , k_w , etc., are given, therefore, with the experimentally determinable constants $k_a' = k_a'' = 0.5 k_a$; with mixed oxides, they remain unknown.

The question is now whether from the constants of the two pure oxides XOX and X'OX', one may infer the constants of the mixed oxides XOX'.

This is readily possible in the limiting case that the reactive groups react uninfluenced and independent of one another. If, therefore, the X is saponified out, at the same group rate, from the XOX, as from the XOX', and the X', at the same group rate, from the X'OX', as from the XOX', then:

$$\left. \begin{aligned} k_a &= 0.5(p_a + q_a), \\ k_s &= 0.5(p_s + q_s), \\ k_w &= 0.5(p_w + q_w), \end{aligned} \right\} \quad (19)$$

where the indexed k designates the constants and mixed oxide, and p and q, the constants of the two pure oxides.

Equations (19) state that the rate is equal to the sum of the group rates or that the rate of the mixed oxide is equal to the arithmetic mean from the rates of the two pure oxides.

If one tests the equations (19) with the aid of the measurements, then it is evident that they are not fulfilled in reality. If we take ethyl acetate as an example, then k would signify the saponification constant of this ester; p, the constants of acetic acid anhydride; q, the constants of ethyl ether. It is true that only the water constant of the anhydride is not known from the constants of the two pure oxides, according to the value, but one knows, with certainty, that q_a is very small, in comparison to p_a , and q_w , in comparison to p_w , and very probably, also q_s , in comparison to p_s . From this and from (19), it would follow that ethyl acetate should react half as

rapidly as the acetic anhydride on all three saponification paths. Not just that this is, by far, not true, but that the reciprocal ratios of the three saponification constants are quite different with the ester from the anhydride was further shown above.

Now, acetyl and ethyl are two groups lying far from one another, and it is perhaps to be expected from the very beginning that the condition which is the basis of the equations (19) is fulfilled all the better, the more similar, in a chemical sense, the two groups bonded on the bridging oxygen behave. We can cite as such a case the mixed anhydride of acetic acid and propionic acid measured by P. E. Verkade [39]. For 25°, the constants of the water saponification of the three substances are the following:

Acetyl oxide	Propionyl oxide	Mixed anhydride
0.1641	0.0857	0.1206

In this conceivably most favorable case, equation (19) is also fulfilled only in a very approximate manner:

$$0.5(0.1641 + 0.0857) = 0.1249 \sim 0.1206.$$

The two groups bound on the bridging oxygen -O- thus do not react independently of one another; they influence each other.

That was rather predictable according to the experience gained up to now with the esters of dibasic acids and diacidic alcohols. According to this experience, the condition of the uninfluenced reaction of two groups is all the better fulfilled, the longer the atom chain which links the two reactive groups with one another. The shortest chain which revealed a still uninfluenced reaction of the ligands in three cases (acidic saponification of oxalic acid ester, acidic and alkaline saponification of ethylene glycol ester) was the following chain:



whereas already the following chain (case of carbonic acid ester and orthoformic acid ether):



produced an extraordinarily strong reciprocal influencing of the ligands. Thus, one should expect, all the more, the latter for the chain -O-.

Instead of the equations (19), therefore, equations of the following form:

$$k = 0.5(pf + qg) \quad (20)$$

have to appear, where f and g are factors which manifest numerically the reciprocal influence of the groups X and X' in XOX'. The factors must be created in such a way that they approximate the value one to the extent that X and X' approximate identity, so that for X' = X, f = g = 1, in which limiting case (20) goes over into (19).

One will be able to progress in the search for corresponding functions for f and g when the three constants of a larger number of pure ethers and pure anhydrides and the corresponding mixed oxides become known some day. For the time being, there is only one single case where testing is possible: the already mentioned water saponification of acetic acid-propionic acid anhydride. Here it is possible to bring (20) in the following form:

$$k_w = 0.5 \left(p_w \sqrt{\frac{\delta_2}{\delta_1}} + q_w \sqrt{\frac{\delta_1}{\delta_2}} \right),$$

where δ_1 is the dissociation constant of the acid of the pure anhydride with the saponification constant p_w and δ_2 has the analogous meaning.

If one sets $\delta_1 = 1.82 \times 10^{-5}$ and $\delta_2 = 1.31 \times 10^{-3}$, then:

$$k_w = 0.5 (0.1641 \times 0.8484 + 0.0857 \times 1.1787) = 0.1201,$$

that is, within the errors, identical with the experimentally found value $k_w = 0.1206$.

Since acetic acid and propionic acid are chemically very close, this agreement is temporarily not yet able to say very much.

The task of chemical kinetics must be to calculate in advance the rate of the saponification of all esters from as few natural constants as possible. If one considers that, as it was possible to show recently [40], in addition to the chemical nature of the reacting substances, their concentration is also decisive for the degree of the independence of the reacting groups and that the "constants" of the reaction rate are approximately constant only over small ranges, one will not be able to avoid agreeing with E. Faerber [41], who stated: "Every explanation, even that of a chemical reaction, is a never-ending task."

The saponification of the formic acid ethyl ester

The hydrolysis of methenyl glycerol ethyl ether to formic acid ester:



is followed by the saponification of the latter to formic acid:



Whereas the first reaction takes place at a noticeable rate only under the catalytic influence of the hydrogen ion and therefore is a typical ether saponification, the second reaction is catalyzed just as well by hydrogen ions, such as the hydroxy ion--that is, belongs to the class of ester saponifications.

* This form is closely related to Verdade's "reduced hydration constants."

Accordingly, there is an acidic and an alkaline saponification constant of reaction (2). The former was determined in the preceding as:

$$k_s = 0.192$$

The constant of the alkaline saponification was measured up to now according to two electrochemical methods and purely chemically, with the aid of an iodide-iodate solution as a hydrogen ion buffer.

In the latter solution, the reaction proceeds more slowly than desired. In an ammonia-ammonium salt solution, the rate can be measured at leisure, but there are concerns regarding this method, since secondary reactions with the formation of amide are not improbable. The even stronger alkaline reaction of the carbonate-bicarbonate buffer makes possible the measurability only with a large addition of bicarbonate. Under these conditions, those evils to which reference was already made in great detail have to be accepted. Nevertheless, taking into consideration that better methods are not known at the time, it appeared recommendable to measure the reaction in this way also.

The execution and calculation of the experiment was done in the same way as in the past [42].

Experiment 12

t	$a-x$	k_s
0	0.0592	---
8	0.0506	0.17
21	0.0362	0.19
46	0.0263	0.16
215	0.0080	0.19
(1) Mittel...		0.18

Key: 1 Average

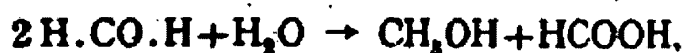
Using 6×10^{-11} for the second dissociation constant of the carbonic acid, $[\text{OH}^-] = 1$:

$$k_a = 1080,$$

a value is calculated which agrees sufficiently with the one found in the iodide-iodate solution, when one considers that the acidities in which the work was carried out here and there differ by three powers of ten.

The high value of k_a corresponds to the strength of the formic acid. The view that an ester saponifies, as a rule, all the more rapidly, the stronger its carboxylic acid, has been repeatedly expressed and as a whole, more or less confirmed by experience. On the other hand, the high value k_s of the acidic saponification is striking. The formic acid esters saponify acidically 20 to 30 times more rapidly than the acetic acid esters and homologs. The large k_s can be related with the acid strength, since the esters of much stronger acids than formic acid saponify acidically more slowly than the formic acid ester. The high value of k_s appears rather to be based in the chemical nature of the formic acid.

In fact, the formic acid is, both according to its behavior and its formula, just as much carboxylic acid (hydrogen carboxylic acid) as aldehyde (oxyformaldehyde). For the aldehyde nature of the formic acid, there is its easy oxidizability, which is completely in contrast to the difficulty with which acetic acid oxidizes; also the circumstance that, similar to the formaldehyde and certain aldehydes:



it is able to give the Cannizzaro reaction:



Formic acid

Formaldehyde

Carbonic acid

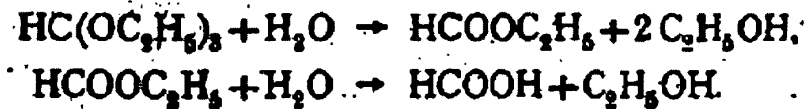
namely, if some of their salts are rapidly heated, and finally, the additional circumstance that according to M. Prud'homme [43] and its thermochemical data, it behaves like a mixture of carboxylic acid and aldehyde alcohol.

One will therefore hardly be mistaken if the rapid alkaline saponification of ethyl formate is attributed to its ester nature (formic acid ester), and the rapid acidic saponification, to its ether nature (ethoxy formaldehyde). As was shown in the preceding, the rapid acidic saponification is characteristic for the reactive ether. As an ether of a secondary alcohol and in view of the similar atom group as in methenyl glycerol ether, with which it is genetically related, the rapid acidic saponification of the ethoxy formaldehyde is not surprising.

Consequently, we have a substance present in ethyl formate which mediates the transition from esters to reactive ethers in a manner similar to the way phenol ethers form the transition from ethers to reactive esters.

Summary

The hydrolysis rate of orthoformic acid ethyl ether was measured. It takes place via formic acid ester as a comprehensible intermediate stage:



The second reaction is a common ester saponification. Its already known constants of the acidic and alkaline saponification were recently measured. $k_s = 0.192$ and $k_a = 1080$ were found for 25° .

As concerns the first reaction, it was determined that it takes place immeasurably slowly in an alkaline solution. From this it follows that the ethyl orthoformate noticeably hydrolyzes neither by water alone nor under the influence of hydroxy ions.

On the other hand, the reaction takes place immeasurably rapidly in a strongly acidic solution. The production of formic acid from the ortho ether in mineral acid solution must therefore take place at a rate which is equivalent to the rate of the acidic saponification of ethyl formate $k_s = 0.192$. The measurements have confirmed this.

For the measurement of the rapid reaction, a hydrogen ion buffer from primary and secondary phosphate proved to be suitable. For the determination of the reaction progress, the produced formic acid ester was determined by analysis. The latter reacts with the acidity of the phosphate buffer and during the time of the experiments to an only very slight extent. Thus, the process of the hydrolysis of the ortho ether to formic ester was isolated, and at the same time, its course attained in a medium of constant acidity. The measurements produced a first-order reaction and the proportionality between rate and hydrogen ion concentration. The rate constant, relative to $[\text{H}^+] = 1$, has the value $k = 70,000$, which is unusually high in comparison with other acidic saponifications.

Following these experiment results and in connection with pertinent explanations by P. E. Verkade, the saponification of the three substance types, ROR', AOR, AOA' where R signifies alkyls and A acyls, was theoretically discussed and the proper classifications of ethyl orthoformate as ether type was indicated.

References

- [1] See A. Eucken, *Zeitschr. f. physik. Chemie*, 71 (1910), 550; A. Skrabal and A. Sperk, *Monatshefte für Chemie*, 38 (1917); 191; M. H. Palomaa, *Ann. Acad. Scient. Fennicae*, Ser. A. Tonn 4 (1913), No. 2.
- [2] *Zeitschr. physik. Chemie*, 41 (1902). 52. – See also *ibid*, 30 (1899), 593.
- [3] Regarding the applied titration method, see A. Skrabal and E. Singer, *Monatshefte für Chemie*, 49 (1919), 363.
- [4] See, for example, A. Kailan, *Monatshefte für Chemie*, 28 (1907), 1187.
- [5] *Theory of alkaline and acidic titrations*, Stuttgart 1914.
- [6] See A. Skrabal, *Monatshefte für Chemie*, 38 (1917), 29.
- [7] See W. Ostwald, *Journ. f. prakt. Chemie*, [2], 28 (1883), 449.
- [8] See A. Skrabal, *Monatshefte für Chemie*, 35 (1914), 1057.
- [9] See A. Skrabal and E. Singer, *l.c.*
- [10] A. Skrabal and A. Sperk, *l.c.*
- [11] A. Skrabal, *Monatshefte für Chemie*, 38 (1917), 305.
- [12] V. Meyer and P. Jacobson, *Lehrb. organ. Chemie*, 2nd Edition, 1, 2 (Leipzig 1913), p. 62.
- [13] *Chem. Weekblad*, 11, (1914); 754; see also *ibid*. 15 (1918), 203.
- [14] *Ansichten über die organ. Chemie* [View of organic chemistry] (Braunschweig 1878), 281.
- [15] *Zeitschr. f. angew. Chemie*, 26, 1 (1913), 730.
- [16] References in A. Skrabal and A. Matievic. *Monatshefte für Chemie*, 39 (1918), 765; A. Skrabal and E. Singer, *ibid.*, 41 (1920), 339.
- [17] J. J. A. Wijs, *Zeitschr. f. physik. Chemie*, 11 (1893), 492 and 12 (1893), 514; H. v. Euler and J. Laurin, *Arkiv för Kemi, Mineralogi och Geologi*, 7 (1920), No. 30
- [18] References in R. Wegscheider, *Ber. chem. Ges.*, 52 (1919), 235.
- [19] *Ber. chem. Ges.*, 52 (1919), 745.

- [20] Ber. chem. Ges., 51 (1918), 480.
- [21] See, in particular, the investigations of P. E. Verkade in Rec. trav. chim.
- [22] Journ. Chem. Soc., 97 (1910), 732 and 1677. See also B. H. Wilsdon and N. V. Sidgwick, *ibid.*, 103 (1913), 1959.
- [23] Journ. Chem. Soc., 101 (1912), 1708.
- [24] See, among others, J. Volhard, *Lieb. Ann.*, 267 (1892), 51; R. Wegscheider and E. Späth, *Monatshefte für Chemie*, 30 (1909) 841.
- [25] On an estimate of k_a with camphoric acid anhydride, see B. H. Wilsdon and N. V. Sidgwick; *Journ. Chem. Soc.*, 107 (1915), 879.
- [26] *Lieb. Ann.*, 165 (1873), 134.
- [27] Ber. chem. Ges., 10 (1877), 704 and 1902.
- [28] L. Knorr, Ber. chem. Ges., 39 (1906), 1409.
- [29] *Lieb. Ann.*, 192 (1878), 119.
- [30] *Journ. prakt. Chemie*, [2], 37 (1888), 534.
- [31] M. Delepine, *Compt. rend.*, 132 (1901), 331, see also M. Gredski, Ber. chem. Ges., 16 (1883), 512.
- [32] E. Claisan, Ber. chem. Ges. 40 (1907), 3903.
- [33] A. A. Noyes and W. J. Hall, *Zeitschr. physik. Chemie*, 18 (1895), 240.
- [34] See also W. Lippert, *Lieb. Ann.*, 276 (1893), 176.
- [35] W. Ostwald, *Journ. prakt. Chemie*, 29 [2], (1884), 385.
- [36] R. Stoermer and B. Kahlert, Ber. chem. Ges., 34 (1901), 1812.
- [37] L. Bouveault, *Bull. Soc. Chim.*, [3], 19 (1898), 75.
- [38] J. H. van't Hoff, *Lectures on theoretical and physical chemistry*, 2nd Edition, No. 3 (Braunschweig 1903), p. 139.
- [39] *Rec. trav. chim.*, 35 (1913), 79 and 299.
- [40] See A. Skrabal and E. Singer, *Monatshefte für Chemie*, 41 (1920), 339.

- [41] Die Naturwissenschaften, 8 (1920), 322.
- [42] A. Skrabal and E. Singer, Monatshefte für Chemie, 40 (1919), 363.
- [43] Journ. de chim. physique, 16 (1918), 438.

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Über die Hydrolysegeschwindigkeit des Orthoameisensäureäthyläthers

Von

Anton Skrabal, k. M. Akad., und Otto Ringer

(Mit 1 Textfigur)

Aus dem Chemischen Institut der Universität Graz

(Vorgelegt in der Sitzung am 13. Jänner 1921)

Einleitung.

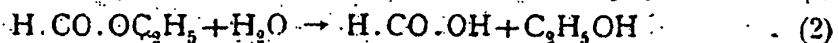
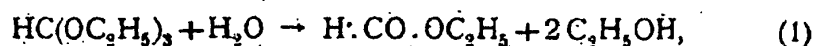
Von der Kenntnis des Zeitverlaufes der einfachen hydrolytischen Reaktionen der verschiedenen Stoffklassen mit ätherartig gebundenem Sauerstoffatom ist die chemische Kinetik noch weit entfernt. So sind auch bis heute die Orthocarbonsäureester, die im Zusammenhang mit wichtigen Konstitutionsproblemen und synthetischen Methoden stehen, hinsichtlich der Kinetik ihrer Hydrolyse in keiner Weise bearbeitet.

Es soll hier mit den Estern der einfachsten Orthocarbonsäure, der hypothetischen Orthoameisensäure, ein Anfang gemacht und die Hydrolyse ihres am leichtesten zugänglichen Esters, des Orthoameisensäureäthylesters $\text{HC}(\text{OC}_2\text{H}_5)_3$, untersucht werden. Nach dem Verhalten dieses Stoffes bei der Hydrolyse, das das Ergebnis vorliegender Untersuchung bildet, wären er und voraussichtlich auch die analogen Verbindungen mit der Atomgruppe $-\text{C}(\text{OR})_3$, wo R ein Alkyl bedeutet, sachgemäßer als Äther und nicht als Ester zu bezeichnen, welche sachgemäßere Bezeichnung bereits im Titel gewählt wurde.

Aus der über diese Verbindung und die nächste homologe, den Orthoessigsäureäther, vorliegenden, ziemlich umfangreichen präparativen Literatur ließ sich nun ein Anhaltspunkt so einwandfrei herausfinden, daß er für unsere Arbeit richtunggebend sein konnte: es konnten bei der Hydrolyse — und zwar ist immer nur von einer durch Säuren bewirkten die Rede — als Abbauprodukte stets

nur Körper mit einer Alkoxygruppe, nämlich die Ester der betreffenden gewöhnlichen Säuren, also der Ameisensäure-, beziehungsweise Essigsäureester, oder deren weitere Zersetzungsprodukte, Säure und Alkohol, vorgefunden werden.

Es durfte daher angenommen werden, daß die Hydrolyse des Orthoameisensäureäthers sich entsprechend den Reaktionsgleichungen



rechnerisch als eine Folgereaktion mit nur einer Zwischenstufe behandeln lassen würde, eine Annahme, die durch das Experiment auch bestätigt wurde.

Die Geschwindigkeit der zweiten Reaktion, der Verseifung des Ameisensäureesters, in ihrer Abhängigkeit von der Konzentration des Esters und den Ionen H^+ und OH^- des Wassers ist bereits bekannt.¹ Festzustellen war also die Geschwindigkeit der ersten Reaktion. Nach den Darlegungen von R. Wegscheider² handelte es sich grundsätzlich um die Ermittlung der Konstanten von drei Nebenreaktionen, der Wasserverseifung, der alkalischen Verseifung und der sauren Verseifung, in welche Konstanten, da in wässriger Lösung gearbeitet wurde, die konstante Wasserkonzentration miteinbezogen werden kann.

Was die Analysierbarkeit des Reaktionsgemisches als Voraussetzung für die Meßbarkeit der Reaktion und die infolge des Reaktionsverlaufes eintretende, die Verseifungsgeschwindigkeit beeinflussende Veränderung der Azidität, anbelangt, so ist folgendes zu sagen. Die erste der beiden Folgewirkungen geht ohne »Säureförmung« vor sich, ihr Verlauf ändert also nichts an der Geschwindigkeit der sauren und alkalischen Verseifung. Die zweite Reaktion macht eine Säure frei, ihr Verlauf verzögert also die alkalische und begünstigt die saure Verseifung. Der Umsatz nach der zweiten Reaktion ergibt sich aus der Titration der gebildeten Ameisensäure, der Umsatz nach der ersten aus der gebildeten Ameisensäure und dem gebildeten Ameisensäureester. Letzterer läßt sich, dank seiner überaus raschen alkalischen Verseifung, durch überschüssiges Alkali, das ihn verseift, und Rücktitrierung mit Säure genau und rasch bestimmen. Voraussetzung für die Anwendbarkeit dieser Analysenmethode ist eine entsprechende Resistenz des Orthoäthers gegenüber Alkali.

Um diese Voraussetzung zu prüfen, war daher zunächst das Verhalten des Orthoäthers in einem entsprechend alkalischen Medium zu untersuchen.

¹ Vgl. A. Eucken, Zeitschr. f. physik. Chemie, 71 (1910), 550; A. Skrabal und A. Sperr, Monatshefte für Chemie, 38 (1917), 101; M. H. Palomaa, Ann. Acad. Scient. Fennicae, Ser. A. Tom 4 (1913), No 2.

² Zeitschr. physik. Chemie, 41 (1902), 52. — Vgl. auch ibid. 30 (1899), 593.

Der benutzte Orthoameisenäthyläther war ein Kahlbaum'sches Präparat, das immer knapp vor seiner Verwendung durch gebrochene Destillation gereinigt wurde. Die Messungen geschahen im Thermostaten bei 25°.

Es wurde also zunächst der Orthoäther in eine Natriumcarbonatlösung gebracht und durch Titration der Soda mit 0.1-norm. HCl zu Bicarbonat die Titeränderung festgestellt. Der Versuch, der sich über eine Woche erstreckte, ergab nur geringe Titerabnahmen. Im Hinblick auf die sehr rasche alkalische Verseifung des Ameisensäureesters können vom letzteren im Reaktionsgemisch nur Spuren zugegen sein. Er muß nach seiner Bildung nach der ersten Reaktion unter den Bedingungen unseres Versuches mit überlegener Geschwindigkeit weiterverseifen. Das Tempo der Titerabnahme wird also wesentlich durch die Geschwindigkeit der Verseifung des Orthoäthers angegeben.

Um zu prüfen, ob die langsame Verseifung des orthoameisensauren Äthyls in der Sodalösung eine Wasserverseifung, eine saure oder eine alkalische ist, wurde der Orthoäther in eine 0.1-norm. Natronlauge gebracht und deren Titerabnahme mit Säure und Phenolphthalein als Indikator ermittelt. In diesem Medium wird der nach Gleichung (1) langsam entstehende Ameisensäureester noch rascher weggefangen als in der Sodalösung und die Titeränderung der Natronlauge gibt direkt den Umsatz des Orthoäthers an. Im Falle der Wasserverseifung war dann dasselbe Tempo wie in der Sodalösung, im Falle der sauren ein verzögertes, im Falle der alkalischen Verseifung ein beschleunigtes Tempo vorauszusagen. Der Versuch ergab Konstanz des Laugentiters während einer Woche. Eine ganz geringfügige Titerabnahme, die eben noch zu beobachten war, ist genügend durch die unvermeidliche Aufnahme von Luftkohlenensäure durch die Natronlauge erklärt.

Somit war einerseits wahrscheinlich gemacht, daß der Orthoäther in der Sodalösung sauer verseift, andererseits festgestellt, daß das orthoameisensaure Äthyl weder einer alkalischen noch auch einer Wasserverseifung unterliegt, jedenfalls nicht im Betrage der sonst bisher vorgefundenen Größenordnungen, eine Einschränkung, die prinzipiell aufzufassen und durch den Grad der Genauigkeit der Analysenmethoden und die Dauer der Messungen bedingt ist.

Wenn die Reaktion in der Sodalösung wirklich eine saure Verseifung sein soll, so war für eine mineralisaure Lösung eine ungeheuer rasche Reaktion des Orthoäthers zu erwarten.

Die Verseifung wurde daher in einer 0.1-norm. salzsauren Lösung untersucht und die Meßmethode so eingerichtet, daß die erste Stufe der Folgewirkungen, die Reaktion des Orthoäthers

¹ Über die angewandte Titrationsmethode siehe A. Skrabal und E. Singer, Monatshefte für Chemie, 40 (1919), 363.

zu Ameisensäureester, bloßgelegt war. Es wurde ein Reaktionsgemisch bereitet, das 0.1 Mole. Äther und 0.1 Mole HCl enthielt, diesem von Zeit zu Zeit Proben entnommen, in Kölbchen, in welche sich eine überschüssige Menge 0.1-norm. Baryt befand, einfließen gelassen und diese mit Korkpfropfen, die Natronkalkröhren trugen, verschlossen.

Die Verseifung des Orthoäthers mußte im Augenblick des Alkalischemachens stillstehen, der aus ihm gebildete Ameisensäureester hingegen, soweit er nicht seinerseits schon sauer verseift war, sehr rasch alkalisch verseifen. Die Titerabnahme der vorgelegten Lauge mußte also nach Abzug des Betrages für die Katalysatorsäure der Summe aus Ameisenester und Ameisensäure und damit der Menge des in der Reaktion verbrauchten Orthoäthers entsprechen.

Die Titerabnahme der Barytlauge zeigte nun stets sowohl bei der sofort nach der Bereitung des Reaktionsgemisches entnommenen Probe, als auch bei allen späteren eine Menge verbrauchten Orthoäthers an, die gleich dessen Anfangskonzentration war. Der Versuch wurde, um ganz sicher zu gehen, wiederholt, immer aber zeigte die erste, gleich zu Beginn der Reaktion entnommene Probe den vollständigen Umsatz des Orthoäthers an.

Die Hydrolyse des Orthoäthers zu Ameisensäureester erfolgt mithin in mineralsaurer Lösung unmeßbar rasch. Dies mußte sich auch auf einem völlig anderen Wege zeigen lassen.

Die Hydrolyse des Ameisensäureesters geht in mineralsaurer Lösung mit mäßiger, genau bekannter Geschwindigkeit vor sich. Wenn Orthoäther in dem sauren Medium reagierte, so lag daher der Fall einer zweistufigen Reaktion vor, bei dem die erste Stufe der zweiten gegenüber mit überragender Geschwindigkeit verläuft, in welchem nicht seltenen Falle, wie zuerst van't Hoff zeigte, der Vorgang durch die einstufige Geschwindigkeitsgleichung der langsameren Teilreaktion dargestellt werden kann. Wurde also dem gleichen Reaktionsgemisch gegenüber eine Meßmethode angewendet, die sich auf die Verfolgung des Umsatzes nach der zweiten Stufe, auf die Messung der gebildeten Ameisensäure gründete, so mußte nach der einstufigen monomolekularen Rechnung die schon bekannte Geschwindigkeitskonstante des Ameisensäureesters herauskommen.

Die Reaktion des Ameisensäureesters und des Orthoameisensäureäthers in salzsaurer Lösung.

Die genaue Messung der Konstante der sauren Verseifung des Ameisensäureesters ist durch Palomaa (l. c.) erfolgt und war mit einer Schwierigkeit verbunden, die wie in vielen ähnlichen Fällen in der raschen alkalischen Verseifung des Esters gelegen ist. Wendet man nämlich zur Bestimmung des Säuretitors Natron und

Phenolphthalein an, so erwächst ein Mehrverbrauch durch die alkalische Verseifung des noch vorhandenen Esters im Titrationsendpunkte und bei dem lokalen Überschuß an Titerlösung an der Einflußstelle.

In solchen Fällen wurde häufig als Maßlösung Ammoniak¹ gewählt, das als schwache Basis diesen Nachteil nicht so zeigt, dafür aber die Titration weniger genau macht. Palomaa suchte den Ausweg in der Mitte, indem er das stärkere Äthylamin verwendete.

Nach der Ausbildung des Titrierverfahrens durch N. Bjerrum² bietet jedoch die Anwendung schwacher Basen und Säuren als Maßlösungen keine Schwierigkeiten, sowie mit den besten, also bestimmten Titrierexponenten gearbeitet wird. Wir benutzten also Ammoniak und 6.35 als den besten Titrierexponenten, für welchen *p*-Nitrophenol ein geeigneter Indikator ist. Der Titrierfehler ist dann 0.03 cm^3 zu Beginn und 0.1 cm^3 zu Ende der Messung oder 1% , beziehungsweise 2% der laufenden Esterkonzentration, entspricht also der erwünschten Genauigkeit.

Auf diese Weise ist die Titrierung des Versuches 1 gemacht worden. Bei den Versuchen 2 bis 5 wurde rascher und einfacher verfahren, indem Alizarin als Indikator benutzt und von Bläßgelb auf Lila titriert wurde.³ Die Genauigkeit dieses vereinfachten Verfahrens ist, wie der Versuch lehrt, ebenfalls eine genügende.

Im übrigen wurde ganz ähnlich wie bei Palomaa vorgegangen, nur wurde die Reaktion in größeren Mengen vorgenommen, indem 500 cm^3 Reaktionsgemisch bereitet und Proben zu 50 cm^3 titriert wurden.

Versuchsreihe I.

Ämeisensäureäthylester in salzsaurer Lösung.

Versuch 1.

$$\xi = 0.09948, S = 0.09934.$$

t	$\xi - x$	k	k
0	0.07970	—	—
15	0.05962	0.0193	0.0193
25	0.04918	0.0192	0.0193
42	0.03516	0.0197	0.0195
60	0.02520	0.0185	0.0192
78	0.01778	0.0193	0.0192
105	0.01072	0.0187	0.0192

Mittel ... 0.0191

k für $S = 1$... 0.0192

¹ Vgl. z. B. A. Kailan, Monatshefte für Chemie, 28 (1907), 1187.

² Theorie der alkal. und azidim. Titrierungen, Stuttgart 1914.

³ Vgl. A. Skrabal, Monatshefte für Chemie, 38 (1917), 29.

Versuch 2.

$$\xi = 0.11255, \quad S = 0.00017$$

t	$\xi - x$	k	k
0	0.10230	—	—
S	0.08844	0.0189	0.0182
16	0.07658	0.0180	0.0181
26	0.06362	0.0186	0.0183
33	0.05102	0.0184	0.0183
54	0.03836	0.0178	0.0182
83	0.02304	0.0176	0.0180

Mittel... 0.0181

 k für $S = 1 \dots 0.183$

Versuch 3.

$$\xi = 0.10835, \quad S = 0.00920$$

t	$\xi - x$	k	k
0	0.10042	—	—
7	0.08844	0.0181	0.0181
14	0.07768	0.0186	0.0183
22	0.06682	0.0188	0.0185
33	0.05474	0.0182	0.0184
50	0.03998	0.0185	0.0184
82	0.02242	0.0181	0.0183
134	0.00873	0.0180	0.0182

Mittel... 0.0183

 k für $S = 1 \dots 0.185$

Versuchsreihe II.

Orthoameisensäureäthyläther in salzsaurer Lösung.

Versuch 4.

$$\xi = 0.12935, \quad S = 0.00788$$

t	$\xi - x$	k	k
0	0.12014	—	—
8	0.10282	0.0195	0.0195
16 ^{45/60}	0.08660	0.0193	0.0194
27 ^{50/60}	0.07002	0.0194	0.0194
40	0.05548	0.0191	0.0193
55	0.04200	0.0186	0.0191
78	0.02740	0.0186	0.0189
118	0.01260	0.0194	0.0191

Mittel... 0.0191

 k für $S = 1 \dots 0.195$

Versuch 5.

$$\xi = 0.10455, \quad S = 0.09831.$$

t	$\xi - x$	k	k
0	0.09652	—	—
7	0.08428	0.0104	0.0104
15	0.07248	0.0189	0.0191
26	0.05880	0.0190	0.0191
39	0.04630	0.0184	0.0188
56	0.03354	0.0190	0.0189
77	0.02258	0.0188	0.0189

Mittel... 0.0189

 k für $S = 1$... 0.192

In den Tabellen bedeutet S die Konzentration der Katalysatorsäure (Salzsäure), die, wie alle übrigen Konzentrationen, in Molen pro Liter angegeben ist, ξ die Gleichgewichtskonzentration der gebildeten Ameisensäure oder der verseifbare Anteil des Esters,¹ $\xi - x$ die aus dem laufenden Säuretiter und ξ und S ermittelte laufende Konzentration des verseifenden Esters und t die Zeit in Minuten.

Die Geschwindigkeitskonstante wurde nach der Formel

$$k = \frac{1}{t_2 - t_1} \ln \frac{\xi - x_1}{\xi - x_2},$$

und zwar einmal aus je zwei unmittelbar aufeinanderfolgenden Werten von t und $\xi - x$, also nach der Schrittformel,² und das andere Mal in der meist üblichen Weise nach der die Fehler abschleifenden Sprungformel berechnet.

Der Mittelwert der auf $S = 1$ bezogenen Konstanten der sauren Verseifung des Ameisensäureesters aus allen drei Versuchen beträgt 0.187 und stimmt mit dem von Palomaa gefundenen vollkommen überein. Als bester Wert soll jedoch der des Versuches 1 gelten, da er auf dem genauesten Titrationsverfahren (Titration mit einem bestimmten Titrierexponenten) fußt. Wir wollen also an dem Wert festhalten:

$$k = 0.192 \text{ (25°)}.$$

Die Versuche 4 und 5 mit dem Orthoameisensäureäthyläther ergaben endlich eine gute Konstanz von k und für den auf $S = 1$ bezogenen Wert der Konstante im Mittel $k = 0.193$, also denselben Wert wie der Ameisensäureäthylester.

¹ Vgl. W. Ostwald, Journ. f. prakt. Chemie, [2], 28 (1883), 449.

² Vgl. A. Skrabal, Monatshefte für Chemie, 35 (1914), 1057.

Damit erscheint es bewiesen, daß der Orthoameisensäureäthyläther in stark saurer Lösung unmeßbar rasch in Ameisensäureester übergeht.

Versuchsplan für die Messung der raschen Reaktion.

Weil die Reaktion (1) in Lösungen $[H] = 0.1$ unmeßbar rasch geht, in Lösungen $[OH] = 0.1$ oder $[H] = 10^{-13}$ aber so gut wie still steht, war vor auszusehen, daß sie bei einer mittleren Azidität mit einer leicht meßbaren Geschwindigkeit vorwärts schreitet. Es war ferner naheliegend, durch Anwendung verschiedener Wasserstoffionpuffer die geeignetste Azidität aufzusuchen.

Um die saure Verseifung des Orthoäthers zu verlangsamen, wurde sie zunächst in dem Reaktionsgemisch (Grammformelgewichte pro Liter)



also bei der Azidität $[H] = 7.2 \times 10^{-6}$ vorgenommen. Die Meßmethode war dieselbe wie die zu Anfang gehandhabte: Auffangen einer Probe in überschüssiger Lauge und Messung des aus dem Orthoäther gebildeten Ameisenesters. Die erste, sofort nach Inangasetzung der Reaktion vorgenommene Messung ergab einen Ablauf zu 50%. Die Hydrolyse ist also auch bei dieser Azidität für die Messung zu rasch.

Damit war ein Fall von Wasserstoffion-Katalyse gegeben von so ungewöhnlicher Geschwindigkeit, wie sie bisher bei sauren Verseifungen noch nicht beobachtet worden war.

Die rasche Verseifung in der Essigsäure-Acetatlösung rechtfertigt neuerdings die eingangs ausgesprochene Vermutung, wonach die in der Sodalösung beobachtete langsame Reaktion eine saure Verseifung sei.

Es wurde kurze Zeit versucht, die Reaktion in einer Carbonatlösung zu messen, wobei zur Erhöhung der Geschwindigkeit ein reichlicher Bicarbonatzusatz angewandt wurde. Tatsächlich war alsdann die Abnahme des Sodatiters eine merklich raschere, abermals ein Zeichen, daß der Orthoäther in der Sodalösung wirklich sauer verseift, doch wurde von jenen Versuchen bald Abstand genommen: Die Reaktion war noch immer zu langsam, um brauchbare Resultate zu geben, und überdies verträgt gerade der Carbonat-Bicarbonatpuffer mit hoher Bicarbonatkonzentration keine Versuchsdauer von vielen Tagen.

Ähnliches gilt für einen Ammoniak-Ammonsalzpuffer, der die Azidität bis $[H] = 10^{-9}$ herabzusetzen erlaubt.

¹ Siehe A. Skrabal und O. Ringer, l. c.

Damit erschienen noch zwei Wege offen, deren Einschlagung ein geeignetes Reaktionstempo versprach: die Wahl eines Puffers mit dem Bereich um $[H^+] = 10^{-8}$ herum oder eines solchen um $[H^+] = 10^{-7}$.

Auch der erstere Weg erwies sich nicht als gut gangbar. Zwar wäre bei $[H^+] = 10^{-8}$ die Aufgabe vom formalen Standpunkte besonders reizvoll gewesen. Wie aus dem schließlich ermittelten Zahlenwert der Konstante des Orthoäthers und den schon bekannten der sauren und alkalischen Verseifung des Ameisensäureesters hervorgeht, wäre die zweistufige Reaktion hier wirklich als solche aufgetreten. Beide Teilreaktionen hätten Geschwindigkeiten gleicher Größenordnung gehabt, die erste wäre die saure Verseifung des Orthoäthers ohne Säuretonung und durch Wasserstoffion beschleunigt, die zweite die alkalische Verseifung — die saure wäre zu vernachlässigen gewesen — des Ameisensäureesters mit Säuretonung und durch Wasserstoffion verzögert gewesen. Der mathematische Ausdruck des ganzen Vorganges wäre ein System simultaner Differentialgleichungen von der Form:

$$\left. \begin{aligned} \frac{dx}{dt} &= k_1 (a-x) \frac{c+y}{b-y} \\ \frac{dy}{dt} &= k_2 (x-y) \frac{b-y}{c+y} \end{aligned} \right\}$$

Ohne auf die Frage der Integration des Systems oder der weiteren Möglichkeiten des Operierens mit diesen Gleichungen einzugehen, kann gesagt werden, daß alle Methoden mathematische Ausdrücke von derartiger Kompliziertheit zur Verfügung gestellt hätten, daß ihre Benützung im Hinblick auf die zu erwartende Genauigkeit der Analysenergebnisse von sehr fraglichem Werte erschien. Der gleichzeitig anwesenden Puffersalze wegen müßte nämlich zur Bestimmung des Ameisensäureesters ein großer Alkaliüberschuß genommen werden, so daß sich $x-y$ als kleine Differenz, also nur wenig genau ermittelt. Überdies mangelt es gerade in dem Gebiete $[H^+] = 10^{-8}$ an einem Puffer von normaler Brauchbarkeit.

In diesem wie in vielen ähnlichen Fällen ist die Hinarbeitung auf möglichst einfache und durchsichtige Verhältnisse dringend geboten. Solche liefert die Azidität $[H^+] = 10^{-7}$, also die Messung der Reaktion im Neutralitätsgebiete.

Hier steht ein Phosphatpuffer aus primärem und sekundärem Phosphat zur Verfügung. Die Dissoziationskonstante der Phosphorsäure nach der zweiten Stufe ist 1.95×10^{-7} oder mit hinreichender Genauigkeit 2×10^{-7} , die Umgebung einer Wasserstoffionkonzentration dieses Zahlenwertes war also in Betracht zu ziehen. Die alkalische Verseifung des Ameisensäureesters mußte, wie eine Überschlagsrechnung ergab, hier schon sehr langsam erfolgen. Damit

Könnte eine sehr wesentliche Vereinfachung der Verhältnisse angestrebt werden. Verließ hier die Reaktion des Orthoäthers so rasch, daß für die Dauer des verfolgten Reaktionsablaufes die die Azidität beeinflussende Verseifung des Ameisenesters vernachlässigt werden durfte, so war eine Isolierung der Reaktion der ersten Stufe, um die es sich ja handelt, und die ohne Säurelösung verläuft, in einem Medium konstanter Azidität erreicht, mithin auf den zu messenden Zeitvorgang das einfachste Zeitgesetz, die einstufige Gleichung erster Ordnung, anwendbar.

Von den Reaktionspartnern war hier nur einer zu analysieren, der gebildete Ameisensäureester, und dies konnte nur durch alkalische Verseifung des letzteren durch einen hinzugefügten entsprechenden Überschuß an Lauge, wobei die zu messende Reaktion unter einem zweckentsprechend gebremst wurde, und nachherige Rücktitrierung auf sekundäres Phosphat geschehen.

Um nun zu erfahren, ob diese wünschenswerten Versuchsbedingungen wirklich realisierbar wären, mußte zunächst ein Anhaltspunkt für die Geschwindigkeit, mit der der Orthoäther hier reagiert, gefunden werden, und so wurden zunächst unter Zugrundelegung dieser Annahmen, ohne Rücksicht darauf, ob sie exakt erfüllt sind, einige orientierende Vorversuche bei einem Verhältnisse der Puffersalze 1:1, also bei einer Azidität $[H^+] = 2 \times 10^{-7}$ ausgeführt; so groß konnten die etwaigen Fehler keineswegs sein, um nicht wenigstens die Größenordnung der Reaktionsgeschwindigkeit erkennen zu lassen.

Diese Vorversuche zeigten nun, daß der Reaktionsablauf in der Tat in wenigen Stunden erfolgte, und lieferten als abgerundeten, ungefähren Zahlenwert die Konstante 50000, bezogen auf $[H^+] = 1$.

Nun war es möglich, die ganze Versuchsanordnung auf eine exakte Basis zu stellen. Wie dies erreicht worden ist, soll im folgenden kurz gezeigt werden.

Es sollen bedeuten:

- k Konstante der sauren Verseifung des Orthoäthers für $[H^+] = 1$.
- k_a Konstante der alkalischen Verseifung des Ameisenesters für $[OH^-] = 1$.
- k_2 Dissoziationskonstante der Phosphorsäure nach der zweiten Stufe.
- k_3 Dissoziationskonstante der Phosphorsäure nach der dritten Stufe.
- a Anfangskonzentration des Orthoäthers.
- π " " " primären Phosphats.
- σ " " " sekundären Phosphats.
- k Wasserstoffionkonzentration.
- $w = 10^{-14}$ Wasserkonstante für 25° .
- x Umsatzvariable der ersten Reaktion.
- y " " " zweiten " " "

Für k wurde der Orientierungswert $k = 5 \times 10^4$, für k_a der Wert $k_a = 1400$ benutzt. Weil es sich lediglich um die Ermittlung der besten Versuchsbedingungen handelt, darf man sich mit ungefähren Zahlenwerten begnügen.

Für den Beginn der Reaktion gilt:

$$h = k_2 \frac{\pi}{\sigma} \quad (3)$$

Im Zuge der Reaktion entsteht eine Menge y an Ameisensäure, sie ist stärker als die Phosphorsäure nach der zweiten Stufe und verwandelt y Mole des sekundären Phosphats in primäres Phosphat. Es gilt daher für die laufende Azidität

$$h = k_2 \frac{\pi + y}{\sigma - y} \quad (4)$$

Indem wir h als konstant nach (3) setzen, machen wir einen Fehler F . Er beträgt in Prozenten:

$$F = \frac{k_2 \frac{\pi + y}{\sigma - y} - k_2 \frac{\pi}{\sigma}}{k_2 \frac{\pi}{\sigma}} 100 = \frac{y(\pi + \sigma)}{\pi(\sigma - y)} 100 \quad (5)$$

Um diesen Fehler in einem beliebigen Stadium der Reaktion also für einen beliebigen Wert des x zu ermitteln, bedarf es der Kenntnis der Beziehung zwischen y und x , und, weil F klein sein soll, so darf man sich mit einer annähernden Beziehung begnügen. Die Annäherung, die wir machen und die um so besser erfüllt ist, je kleiner das F oder je unveränderlicher das h ist, besteht darin, daß wir y als klein gegenüber x , π und σ vernachlässigen. Dann vereinfachen sich unsere simultanen Differentialgleichungen und werden:

$$\left. \begin{aligned} \frac{dx}{dt} &= kh(a-x), \\ \frac{dy}{dt} &= k_a \frac{n}{h} x, \end{aligned} \right\} \quad (6)$$

wo h den Wert nach (3) hat.

Hierin folgt durch Division

$$\frac{dy}{dx} = \frac{k_a n}{kh^2} \cdot \frac{x}{a-x}$$

¹ A. Skrabal und A. Sperk, l. c.

und integriert:

$$y = \frac{k_a w}{k h^2} \{a - x - a \ln(a - x)\} + J.$$

Die Integrationskonstante J folgt aus $y = 0$ für $x = 0$. Ihre Einsetzung ergibt schließlich als gesuchte Beziehung:

$$y = \frac{k_b w}{k h^2} \left\{ a \ln \frac{a}{a-x} - x \right\}. \quad (7)$$

Nach diesem Ausdruck können nun die y für beliebige a , x und h berechnet und durch Einsetzung von y in (5) die Fehler- F in ihrer Abhängigkeit von y und den Puffersalzmengen π und σ ermittelt werden.

Dies wurde für eine Reihe von Fällen durchgeführt und es ergaben sich für eine Anzahl von ihnen genügend kleine Werte von F .

Die erhaltenen Resultate wurden für die festzusetzenden Versuchsbedingungen unter Berücksichtigung noch folgender Gesichtspunkte verwertet.

Die einzig mögliche Art der Analyse wurde schon gekennzeichnet. Die Hauptsache war, mit möglichst geringen Laugenüberschüssen auszukommen, wenn das Analysenergebnis als kleine Differenz nicht sehr ungenau sein sollte.

Dem stand entgegen die Anwesenheit der Puffersalze. Je geringere Mengen an Puffersalzen verwendet werden durften, um so geringer durfte die Laugenmenge angesetzt werden. Sie durften jedoch nicht zu gering gewählt werden, denn aus (5) geht hervor, daß F um so kleiner ist, je größer π und σ sind. Zwischen diesen entgegengesetzten Rücksichten mußte also der Mittelweg gesucht und gefunden werden.

Der Laugenüberschuß war so zu bemessen, daß der zu analysierende Ameisenester in kurzer Zeit quantitativ verseift. Bei geringem Laugenüberschuß verseift er zunächst in der überschüssigen Lauge und dann, wenn diese verbraucht, in einem Gemisch von sekundärem und tertiärem Phosphat. Die Reaktionszeit für die Esterverseifung ist reichlich bemessen, wenn wir sie für die Alkalität berechnen, die zu Ende der Reaktion herrscht. Diese Alkalität folgt, entsprechend dem Hydrolysegleichgewicht

$$\frac{[\text{HPO}_4''] [\text{OH}']}{[\text{PO}_4''']} = \frac{w}{k_3},$$

aus der quadratischen Gleichung

$$[\text{OH}'] = \frac{w}{k_3} \cdot \frac{T - [\text{OH}']}{S + [\text{OH}']},$$

oder

$$[\text{OH}]^2 + \left(S + \frac{n}{k_s}\right)[\text{OH}'] - \frac{n}{k_s}T = 0, \quad (8)$$

wo S und T die »analytischen Konzentrationen« des sekundären beziehungsweise tertiären Phosphats bedeuten.

Nehmen wir den Ameisenester als verseift an, wenn er sich zu 99% umgesetzt hat, so berechnet sich für die Alkalität $[\text{OH}]$ die Reaktionszeit R in Minuten nach der Gleichung

$$k_a[\text{OH}]R = \ln 100. \quad (9)$$

Der Laugenüberschuß wurde so bemessen, daß R nur Minutenbruchteile beträgt. Weil der Ameisenester zunächst in einem wesentlich alkalischeren Medium verseift, ist diese Festsetzung sicher viel zu reichlich, man überzeugt sich jedoch bald, daß hier nicht viel zu ersparen ist.

Aus diesen dargelegten Gesichtspunkten wurden nun Reihen von Versuchsbedingungen erwogen und schließlich die folgenden als die geeignetsten gewählt:

	Versuchsreihe A	Versuchsreihe B
α	0.1	0.1
π	0.03	0.06
σ	0.06	0.06
h (3).....	1×10^{-1}	2×10^{-1}
x	0.07	0.09
y (7).....	0.0014	0.00098
F (5).....	7.2	3.3
L	0.14	0.20
S	0.05	0.07
T	0.04	0.05
$[\text{OH}]$ (8).....	0.013	0.013
R (9).....	0.25	0.25

Der nach (5) berechnete, aus der Inkonzanz der Azidität fließende Fehler erscheint hier für jenes x angegeben, bis zu welchem die Reaktion messend verfolgt wurde, also für das Ende der Messung. Für Mitte und Anfang der Messung ist er natürlich wesentlich geringer, so daß die Azidität mit hinreichender Genauigkeit als konstant angenommen werden dürfte.

L ist die zur Fixierung des reagierenden Systems und zur Verseifung des gebildeten Ameisenesters angewandte Laugenmenge. Sie ist, wie die übrigen Konzentrationen, in der Tabelle in Molen pro Liter angeführt.

Die Messung der sauren Verseifung des Orthoäthers.

Die Titration geschah nach den Angaben Bjerrum's zu sekundärem Phosphat, und zwar zu einem Titrierexponenten 9.57 und unter Verwendung einer mit dem Indikator angefärbten Sörensen'schen Standardlösung. Auf 100 cm^3 der letzteren sowie der ausitierten Lösung wurden 13 Tropfen einer einpromilligen alkoholischen Phenolphthaleinlösung benutzt.

Bei diesem Titrierexponenten war eine saure Verseifung des Orthoäthers nicht zu befürchten, hingegen mußte die Anwendung einer starken Säure als Maßlösung vermieden werden mit Rücksicht auf den lokalen Säureüberschuß an der Einflußstelle, der zur sauren Verseifung des Orthoäthers führen konnte. Letztere verläuft ohne Säuretönung, wäre also an sich ohne nachteilige Wirkung, führt jedoch zu Ameisenester, welcher letzterer in der zu titrierenden Lösung alkalisch verseift und einen fehlerhaften Minderverbrauch an Titriersäure herbeiführen würde. Aus diesem Grunde wurde 0.1-norm. Essigsäure als Maßlösung benutzt, was für die Genauigkeit der Titration ohne Belang war, da die Dissoziationskonstante der Essigsäure wesentlich größer ist als k_2 der Phosphorsäure.

Die Durchführung der Versuche geschah folgendermaßen:

Als Puffersalze wurden die Kahlbaum'schen Präparate KH_2PO_4 und $Na_2HPO_4 \cdot 2H_2O$ nach Sörensen verwendet. Die eingewogenen Mengen wurden in einem Maßkolben zu 500 cm^3 in ausgekochtem Wasser gelöst und der mittels einer Rey'schen Pipette eingewogene Orthoäther hinzugegeben, bis zur Marke aufgefüllt, in den Reaktionskolben übergegossen, rasch auf 25° gebracht und der Reaktionskolben in den Thermostaten gehängt.

Der Reaktionskolben war mit einer abschließbaren Hebevorrichtung versehen, die es gestattete, unter möglichst kleinen Verdampfungsverlusten die Proben zu entnehmen. Diese wurden in einem Maßkolben zu 50 cm^3 aufgefangen und von diesem in ein Becherglas gebracht (Zeitablesung), in welches zuvor aus einer automatischen Pipette die erforderliche Menge Lauge gegeben worden war. Nach einigem Zuwarten ($\frac{1}{4}$ Minute, siehe oben) erfolgte die Rücktitrierung mit Essigsäure.

Die Berechnung geschah nach der Formel:

$$kh = \frac{1}{t_2 - t_1} \ln \frac{a - x_1}{a - x_2} \quad (10)$$

Die Methode, wie sie geschildert, ließ keine besondere Genauigkeit erwarten, da trotz aller Einschränkung mit ziemlichen Laugenüberschüssen gearbeitet werden mußte, die laufende Konzentration $a - x$ daher als kleine Differenz herauskam. Dazu treten noch die

unvermeidlichen Fehler, die infolge Einwirkung der Luftkohlenensäure stets mit Arbeiten verbunden sind, bei denen einige Zeit hindurch mit stark alkalischen Lösungen umgegangen werden muß.

Endlich kam noch eine weitere Fehlerquelle in Betracht, deren Einfluß nicht noch weitergehend ausgeschaltet werden konnte, und die den Grad der Genauigkeit um noch eine Stufe herabdrückte. Es war dies die Verdampfung des Ameisensäureesters, der für sich bei 54° siedet und in dem reagierenden Gemisch von 25° einen hohen Teildampfdruck aufweist.

Nun ist dieser Tatbestand der genauen Messung der sauren und alkalischen Verseifung jenes Esters wenig hinderlich. Bei diesen raschen Reaktionen sinkt die Konzentration des flüchtigen Reaktionspartners mit der Zeit rasch ab unter Bildung nichtflüchtiger Reaktionsprodukte, die gemessen werden. Hier aber nimmt die Konzentration des flüchtigen Stoffes mit der Zeit zu und hat die größten Werte gegen Ende, also im zweiten, ungleich längeren Teile der Reaktion, und zur Messung des Reaktionsfortschrittes dient der sich bildende flüchtige Stoff.

Auch die oben erwähnte Art der Probenentnahme konnte diesen Übelstand nur vermindern, nicht aber beseitigen, denn mit der Dauer der Reaktion und der allmählichen Entleerung des Reaktionskolbens wird der Luftraum im letzteren und damit die Verdampfung immer größer.

Der Verlust infolge Verdampfung ist auch aus den Versuchstabellen ersichtlich aus den dort angegebenen Werten für die Zeit Unendlich. Der Ausweg, der in solchen Fällen oft gewählt wird, nämlich der, die laufende Konzentration nicht aus dem Anfangswerte, sondern aus dem Endwerte zu ermitteln, war hier nicht gangbar, weil ja durch die Verdampfung nicht die Konzentration des reagierenden Stoffes, sondern die zu messende des flüchtigen Reaktionsproduktes vermindert wurde.

In den folgenden Tabellen bedeutet a die eingewogene Menge des Orthoäthers, die der Berechnung zugrunde gelegt wurde, x_{∞} die zu Ende der Reaktion durch Analyse gefundene Menge des Ameisenesters. Weil Gegenreaktion sicher nicht vorliegt, hätte $x_{\infty} = a$ erwartet werden dürfen. Infolge Verdampfung wurde $x_{\infty} < a$ gefunden. Die geschilderte Erscheinung gibt sich vor allem in einem starken Absinken der Konstanten im letzten Viertel der Reaktion zu erkennen. In der Versuchsreihe B, deren Reaktionen länger verfolgt wurden, zeigt sich das Gefälle deutlicher als in der Versuchsreihe A. Die infolge der Verdampfung zu klein gefundenen Konstantenwerte wurden in den Tabellen eingeklammert und bei der Berechnung des Mittels weggelassen. Wir lassen nun die Messungen folgen.

A. Skrabal und O. Ringer,

Versuchsreihe A.

$$h = 1 \times 10^{-7}$$

Versuch 6.

$$a = 0.10949, \quad x_{\infty} = 0.10388$$

t	$a-x$	kh	kh
0	0.09859	—	—
25	0.08254	0.0071	0.0071
57	0.06631	0.0069	0.0069
94	0.05195	0.0066	0.0069
153	0.03497	0.0067	0.0068

$$kh = 0.00670$$

Versuch 7.

$$a = 0.11700, \quad x_{\infty} = 0.10576$$

t	$a-x$	kh	kh
0	0.10550	—	—
23	0.08958	0.0071	0.0071
47	0.07684	0.0065	0.0067
82	0.06094	0.0065	0.0067
125	0.04580	0.0066	0.0066
185	0.03210	0.0059	0.0064

$$kh = 0.00664$$

Versuch 8.

$$a = 0.11340, \quad x_{\infty} = 0.10590$$

t	$a-x$	kh	kh
0	0.0952	—	—
21	0.0835	0.0062	0.0062
46	0.0703	0.0069	0.0069
77	0.0564	0.0071	0.0068
118	0.0423	0.0070	0.0069

$$kh = 0.00685$$

Versuch 9.

$$a = 0.11203, \quad x_{\infty} = 0.10448$$

t	$a-x$	kh	kh
0	0.10543	—	—
19	0.09369	0.0062	0.0062
46	0.07637	0.0075	0.0070
77	0.06255	0.0084	0.0068
115	0.04863	0.0086	0.0067
169	0.03433	0.0084	0.0068

$$kh = 0.00669$$

Versuchsreihe B.

$$h = 2 \times 10^{-7}$$

Versuch 10.

$$a = 0.00733, x_{\infty} = 0.08986$$

t	$a-x$	kh	kh
0	0.08405	—	—
15	0.06807	0.0141	0.0141
53	0.03987	0.0141	0.0141
81	0.02665	0.0144	0.0142
117	(0.01847)	(0.0102)	(0.0129)
166	(0.01259)	(0.0078)	(0.0114)

$$kh = 0.01415$$

Versuch 11.

$$a = 0.10527, x_{\infty} = 0.09621$$

t	$a-x$	kh	kh
0	0.08927	—	—
9	0.07903	0.0135	0.0135
20	0.06705	0.0149	0.0143
34	0.05535	0.0137	0.0141
69	0.03541	0.0127	0.0134
100	(0.02451)	(0.0119)	(0.0129)
136	(0.01709)	(0.0120)	(0.0120)

$$kh = 0.01373$$

Die erste Reihe kh wurde immer durch intervallweise Integration, die zweite durch Integration von Anfang an berechnet. Die Mittelwerte von kh wurden aus allen Kombinationen aller nicht eingeklammerten Meßergebnisse errechnet.

Die Konstanz von kh innerhalb der einzelnen Versuche konnte nach den angeführten Fehlerquellen nicht besser erwartet werden.

Die Werte der Versuchsreihe A geben ihrerseits als Mittel

$$kh = 0.00674 \quad (h = 1 \times 10^{-7})$$

und die zwei der Versuchsreihe B

$$kh = 0.01394 \quad (h = 2 \times 10^{-7})$$

Sie stehen also ebenso wie die Azidität im Verhältnisse 1:2 mit einer Abweichung von nur etwa 3%.

Damit erscheint nachgewiesen, daß sich die Hydrolyse des Orthoameisensäureäthyläthers zu Ameisensäureäthylester als eine einstufige Reaktion berechnen läßt, deren Geschwindigkeit der Konzentration von Orthoäther und Wasserstoffion proportional ist.

Bezieht man die Geschwindigkeit auf die Konzentrationseinheit von Orthoäther und Wasserstoffion, so erhält man 6.85×10^4 oder abgerundet:

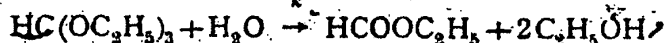
$$k = 70000 \quad (25^\circ).$$

Hieraus folgt für $[H^+] = 0.1$ eine Halbierungszeit von 1×10^{-4} Minuten oder — für den Ablauf zu 99% — eine Reaktionszeit von 6×10^{-4} Minuten, im Einklange mit dem Ergebnisse der Messungen in 0.1-norm. HCl-Lösung.

Auch die Ergebnisse der Vorversuche stimmen mit dem Zahlenwert der Konstante überein. Auf der einen Seite berechnen sich nämlich aus ihr für die Halbierungszeit in dem Essigsäure-Acetat-Versuch ($k = 7 \times 10^{-6}$) 1 Minute, auf der anderen Seite für den Ablauf zu nur 10% eine Reaktionszeit von 20 Tagen für den Carbonat-Bicarbonat-Versuch ($k = 6 \times 10^{-11}$) und von 10000 Tagen für die Hydrolyse durch 0.1-norm. NaOH ($k = 10^{-13}$).

Über die chemische Natur des Äthylorthofor miats.

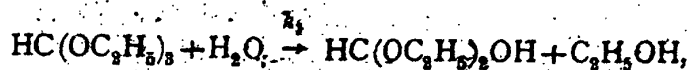
Nach dem Ergebnis unserer Messungen reagiert sonach der Orthoameisensäureäther im Sinne der Gleichung



mit einer Geschwindigkeit k , die der Wasserstoffionkonzentration proportional ist. Für $[H^+] = 1$ hat k den ungeheuren Wert von 70000.

Ob diese rasche saure Hydrolyse direkt, in einem Zuge, oder über Zwischenstufen verläuft, diese Frage bleibt unentschieden. Beide Annahmen sind mit dem Ergebnis der Messungen verträglich. Das „chemische Gefühl“ spricht für den Stufenverlauf. Die Neigung, Stufenreaktionen im vorliegenden Falle und in ähnlichen Fällen anzunehmen, entspricht unseren derzeitigen molekular-kinetischen, auf wahrscheinlichkeitstheoretischen Anschauungen beruhenden und auf allgemeine Erfahrungen sich stützenden Vorstellungen.

Folgen wir dieser Neigung, so hätten wir mindestens zwei Stufenreaktionen anzunehmen:

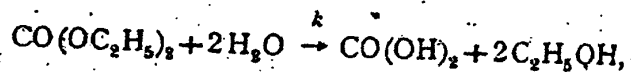


wö zwischen k_1 und k_2 Beziehungen gelten müssen, die so geartet, daß sich meßnerisch die Stufenfolge mit den Konstanten k_1 und k_2 genau so wie die direkte Reaktion mit der Konstanten k verhält. Es sind zwei Beziehungen, die dieser Bedingung Genüge leisten.

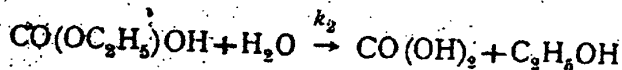
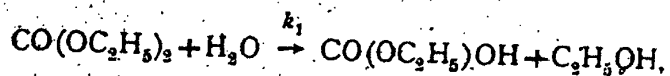
1. Fall. Die Konstante k_1 ist sehr groß gegenüber k_2 . Der Orthoameisensäureäther geht relativ rasch in den Zwischenstoff $\text{HC}(\text{OC}_2\text{H}_5)_2\text{OH}$ über und was gemessen wird, ist die Umwandlung des letzteren in Ameisenester. Die gemessene Konstante k ist $k = k_2$. Gegen diese Hypothese spricht der Umstand, daß der Zwischenstoff bisher weder isoliert noch nachgewiesen werden konnte. Weil sich im alkalisch gemachten Medium weder Ameisenester noch seine Verseifungsprodukte bilden, kann k_2 in diesem Medium nur sehr klein sein. Durch Auflösung des Orthoäthers in verdünnter Säure und sofortige Alkalisierung der Lösung müßte sich der Orthoäther so gut wie vollständig in das Zwischenprodukt verwandeln und letzteres sich sodann nachweisen und z. B. durch Vakuumdestillation isolieren lassen. Daß dies der präparativen Kunst noch nicht gelungen, spricht gegen die Annahme $k_1 \gg k_2$.

2. Fall. Die Konstante k_1 ist sehr klein gegenüber k_2 . Der Orthoäther bildet relativ langsam den Zwischenstoff $\text{HC}(\text{OC}_2\text{H}_5)_2\text{OH}$, der sich seinerseits relativ rasch zu Ameisenester umsetzt. Die gemessene Konstante k ist $k = k_1$. Daß sich der Zwischenstoff noch nicht nachweisen, geschweige denn isolieren ließ, spricht zugunsten der Annahme $k_1 \ll k_2$.

Aber auch direkte Beobachtungen, die an einem anderen Stoffe gemacht worden sind, welcher an denselben Kohlenstoff Hydroxyl und Alkoxyl gebunden hat, sprechen für $k_1 \ll k_2$. Wir meinen die Verseifung der Kohlensäureester.¹ Auch diese Reaktion verläuft nach den Messungen wie eine einstufige Reaktion



die ebenso wie die Hydrolyse des Ameisensäureorthoäthers in die Stufenfolge



zerlegt gedacht werden kann. Hier hat man es aber in der Hand, die zweite der beiden Stufenreaktionen bloßzulegen, indem sich der Zwischenstoff in Form seines Natriumsalzes darstellen und in bezug auf seine Reaktionsfähigkeit direkt untersuchen läßt. Bringt man dieses Natriumsalz in wässrige Lösung, so lehrt der Versuch,

¹ A. Skrabal, Monatshefte für Chemie, 38 (1917), 305.

daß es unter allen Verhältnissen, d. h. bei jeder in Betracht kommenden Azidität, so gut wie momentan zu Kohlensäure und Alkohol reagiert.

Wenn wir demnach, der allgemeinen Neigung folgend, die meßbare Reaktion der Verseifung der Kohlensäureester in eine Stufenfolge zerlegen, so sind, was die Konstanten der Stufenfolge anbelangt, notwendig an diese Zerlegung als weitere Bedingungen $k_1 \ll k_2$ und $k = k_1$ geknüpft.

Die Verhältnisse beim Kohlensäureester sowie der weitere Umstand, daß ganz allgemein die Monoalkyl- und Monoacylderivate der Geminal-Glykole meist schwer zu fassen sind,¹ sprechen dafür, daß wir auch für die Stufenfolge der Orthoameisensäureätherhydrolyse $k_1 \ll k_2$ und $k = k_1$ als wahrscheinlich anzunehmen haben.²

¹ V. Meyer und P. Jacobson, Lehrb. organ. Chemie, 2. Aufl., I, 2 (Leipzig 1913), p. 62.

² Molekularkinetisch ist damit folgendes gesagt. Es handelt sich um die stufenweise Reaktion eines Stoffes mit zwei identischen und identisch gebundenen reaktionsfähigen Gruppen X. Ein solcher Stoff hat das Formelbild $XAAX$. Er reagiert nach dem Stufenschema:



Bezeichnet x die Konstante der Gruppengeschwindigkeit des Stoffes $XAAX$, d. h. die Geschwindigkeit, mit welcher eine bestimmte Gruppe X dieses Stoffes reagiert, so ist die Geschwindigkeit k_1 , mit welcher die eine oder die andere Gruppe in $XAAX$ reagiert, $k_1 = 2x$. Was alsdann die Geschwindigkeit k_2 nach der zweiten Stufe anbelangt, so sind hier drei Fälle zu unterscheiden:

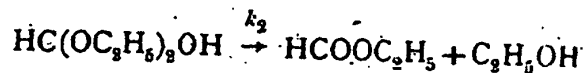
1. Die Reaktion der Gruppe X erfolgt unabhängig, d. h. (vgl. R. Wegscheider, Monatshefte für Chemie, 29 (1908), 91, und 36 (1915), 471) unbeeinflusst davon, ob die zweite Gruppe X noch vorhanden oder schon durch Z ersetzt ist. Dann ist $k_2 = x$.

Dieser Fall ist u. a. realisiert bei der sauren Verseifung und Veresterung der normalen Oxalsäurehomologen und der Weinsäure und bei der sauren und alkalischen Verseifung der Ester des Äthylenglykols. Bei der elektrolytischen Dissoziation zweiwertiger symmetrischer Säuren und Basen liegt er vor, wenn das Verhältnis $\delta_1 : \delta_2$ der Konstanten der stufenweisen elektrolytischen Dissoziation 4 ist, was annähernd beim Phenolphthalein und beim Krystallviolett zutrifft, denn zwischen $\delta_1 : \delta_2$ und den Verhältnissen der kinetischen Konstanten der Stufenfolgen der elektrolytischen Dissoziation besteht ein Zusammenhang:

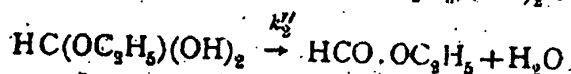
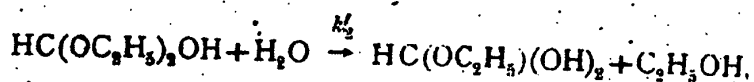
2. Die Reaktionsfähigkeit der Gruppe X ist eine abhängige, in der Weise, daß das X langsamer reagiert, wenn das andere X schon reagiert hat, also durch Z ersetzt ist. Dann ist $k_2 < x$. Dieser Fall scheint die Regel zu bilden. Er ist beispielsweise realisiert bei der alkalischen Verseifung der Ester der normalen Oxalsäurehomologen und der Weinsäure. Er ist ferner verwirklicht bei der stufenweisen elektrolytischen Dissoziation der symmetrischen Säuren und Basen, indem $\delta_1 : \delta_2$ in der Regel größer, sehr häufig sehr viel größer als 4 ist. (Vgl. E. Q. Adams, Journ. Am. Chem. Soc., 38 (1916), 1503).

3. Die Reaktion der Gruppe X ist eine abhängige, in der Weise, daß das X rascher reagiert, wenn das andere X bereits reagiert hat. Dann ist $k_2 > x$. Dieser Fall ist bei der Verseifung der Kohlensäureester realisiert. Er scheint vielleicht ganz allgemein bei der Verseifung der Äther und Ester der Geminalglykole verwirklicht zu sein.

Analog wie beim Kohlensäureester kann auch bei unserem Orthoäther die rasche Reaktion nach der zweiten Stufe entweder das Ergebnis eines intramolekularen Vorganges:



oder das einer weiteren Stufenfolge:



sein, worüber nicht entschieden zu werden vermag.

Eine andere, auf Grund unseres reaktionskinetischen Befundes zu erörternde Frage ist die nach der Charakterisierung der chemischen Natur des Äthylorthoformiats. In dieser Hinsicht ist jedenfalls zu sagen, daß letzteres aus der Klasse der Ester auszuscheiden und in die Gruppe der Äther einzureihen ist.

Bezeichnet R ein Alkyl, A ein Acyl, so lassen sich hinsichtlich des Vorganges der Hydrolyse sowie der ganzen übrigen chemischen Charakteristik drei Typen von Stoffen mit ätherartig gebundenem Sauerstoffatom feststellen:

- Typus I. (Äther): ROR'
 II (Ester): AOR
 III (Anhydride): AOA'

Diese Trennung wird als keine prinzipielle, sondern wahrscheinlich nur als eine graduelle aufzufassen sein, denn, wie P. E. Verkade¹ gezeigt hat, besteht zwischen Carbonsäure einerseits, Alkohol andererseits weitgehende Übereinstimmung und hinsichtlich des chemischen Verhaltens der beiden Stoffklassen — wenn man von den spezifischen Reaktionen der Carbonsäuren, die durch die Carbonylgruppe bedingt sind, absieht — kein grundsätzlicher Unterschied.

Wenn auf der einen Seite eine Analogie zwischen Acyl und Alkyl besteht, so besteht auf der anderen Seite eine solche zwischen Alkyl und Wasserstoff. Die Auffassung des Wasserstoffatoms als einfachstes Alkyl der Grenzkohlenwasserstoffe reicht bis auf J. H. van't Hoff² zurück und wurde vor einiger Zeit namentlich von K. Kubierschky³ überzeugend dargetan. Unsere Übersicht schließt daher die freien Carbonsäuren als Grenzfälle der Ester und die Alkohole und das Wasser als Grenzfälle der Äther ein. Die

¹ Chem. Weckblad, 11 (1914), 754; vgl. auch ibid. 75 (1918), 203.

² Ansichten über die organ. Chemie (Braunschweig 1878), 281.

³ Zeitschr. f. angew. Chemie, 26, I. (1913), 730.

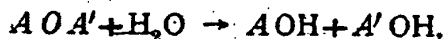
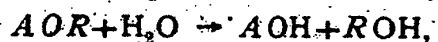
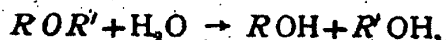
wichtige Reaktion der Verseifung oder Hydrolyse erweist sich alsdann als ein Fall von »Umesterung«, worunter man die Erscheinung versteht, daß die Stoffe mit einem Äthersauerstoff in Reaktion mit anderen Stoffen mit Äthersauerstoff ihre Acyle und Alkyle auszutauschen vermögen.

Geht man von mehrwertigen Alkoholen und Carbonsäuren sowie den Zwittergebilden, den Oxycarbonsäuren, aus, so vermögen diese Stoffe neben den »äußeren« auch innere Äther, Ester und Anhydride zu bilden. Die Carbonylverbindungen beispielsweise sind alsdann als innere Äther der Geminalglykole aufzufassen. In unsere Übersicht fallen somit alle organischen Verbindungen mit einem Sauerstoffatom, dessen zwei Valenzen an C oder H gebunden sind.

Andere organische Verbindungen lassen sich wieder, von unseren drei Typen ausgehend, in der Weise abgeleitet denken, daß man schrittweise R, A, RO, AO oder O durch andere analoge Elemente oder Elementgruppen ersetzt, wodurch man zu Verbindungen gelangt, die in bezug auf Verhalten und Synthese nähere oder fernere Analogie mit den Äthern, Estern und Anhydriden zeigen. Auf diesem Wege gelangt man zu einer Systematik der organischen Verbindungen, als deren Urtyp sich der allgemeinste unserer drei Typen, der Estertypus, hinstellt.¹

Bestehen also deutliche Übergänge und Kontinuitäten, so empfiehlt es sich dennoch im Interesse der Klassifikation und Einreihung der einzelnen Stoffe in zusammengehörige Gruppen, vornehmlich das Unterschiedliche und Trennende hervorzuheben. Das Aufzeigen der Kontinuitäten und die Aufsuchung der Gesetze ihrer Abstufung sind Aufgaben der späteren Entwicklung.

Zu den Reaktionen unserer drei Stofftypen, die auch quantitativ untersucht und also am genauesten bekannt sind, gehört der Vorgang der Hydrolyse oder Verseifung nach den Reaktionsgleichungen:



welche Reaktionen in entsprechend starker Verdünnung mehr oder weniger vollständig verlaufen.

¹ Es wäre von großem Reiz, auf die »Estersystematik« der organischen Stoffe des näheren einzugehen. Ich will dies vertagen, bis mehr experimentelles Material, vor allem Geschwindigkeitsmessungen, vorliegen werden. Die »Reaktionsfähigkeit« der Stoffe, die »Beweglichkeit« der Atome und Gruppen finden in den Geschwindigkeitskonstanten ihren exakten Ausdruck, wobei zu berücksichtigen ist, daß bekanntlich das Stattfinden oder Ausbleiben einer denkbaren Reaktion in der organischen Chemie weit häufiger als durch energetische Momente durch kinetische bedingt wird, woraus die Bedeutung der chemischen Kinetik für die organische Chemie hervorgehen mag. (A. S.)

Der aus dem allgemeinen Streben nach einer möglichst einheitlichen Darstellung alles Naturgeschehens hervorgegangene Grundsatz der chemischen Kinetik, alle möglichen Reaktionen als auch wirklich erfolgend anzusehen, führt uns dazu, für den Vorgang der Hydrolyse bei unveränderlicher Wasserkonzentration das allgemeine Zeitgesetz einer Nebenwirkung anzunehmen:

$$-\frac{dV}{dt} = k_a [\text{OH}'] V + k_s [\text{H}'] V + k_w V, \quad (11)$$

wo V die Konzentration des hydrolysierenden Stoffes bedeutet. Die drei Geschwindigkeitskonstanten k_a , k_s , k_w sollen als die Konstanten der alkalischen Verseifung, der sauren Verseifung und der Wasserverseifung bezeichnet werden.

Die Konzentrationen $[\text{OH}']$ und $[\text{H}']$ sind voneinander nicht unabhängig, sondern durch die Beziehung verknüpft:

$$[\text{H}'] [\text{OH}'] = w, \quad (12)$$

wobei zu bemerken ist, daß die zu dieser Gleichgewichtsbedingung führenden Reaktionen erfahrungsgemäß mit überragender Geschwindigkeit sich einstellen, so daß die Beziehung (12) immer erfüllt ist.

Aus (11) und (12) ist ohneweiters ersichtlich, daß bei einer bestimmten Azidität die Verseifungsgeschwindigkeit $-dV/dt$ ein Minimum sein muß. Wir erfahren die Minimumbedingung, wenn wir nach Einsetzung von $[\text{OH}']$ aus (12) in (11) letztere Gleichung nach $[\text{H}']$ differenzieren und die Ableitung gleich Null setzen, wobei wir bekommen:

$$[\text{H}'] = \sqrt{w \frac{k_a}{k_s}} \quad (13)$$

Man kann die Bedingung (13) auch in der Form schreiben:

$$\frac{[\text{H}']}{[\text{OH}']} = \frac{k_a}{k_s}, \quad (14)$$

die besagt, daß die Verseifungsgeschwindigkeit ein Minimum ist, wenn sich $[\text{H}']$ zu $[\text{OH}']$ wie die Konstante der alkalischen zur Konstante der sauren Verseifung verhält.

Denken wir uns die Verseifung bei konstanter Azidität, etwa durch einen geeigneten Puffer geregelt, verlaufend, so ist ihre Minimalgeschwindigkeit durch die Gleichung gegeben:

$$-\frac{dV}{dt} = 2k_m V + k_w V, \quad (15)$$

wo k_m die Bedeutung hat:

$$[\text{OH}'] k_a = [\text{H}'] k_s = k_m. \quad (16)$$

Auf der anderen Seite gibt es zwei Höchstwerte der Geschwindigkeiten der Verseifung, deren Bedingungen man sich durch Anwendung möglichst alkalischer, beziehungsweise möglichst saurer Lösungen nähern kann, in diesem Vorhaben aber theoretisch und praktisch auf Grenzen stößt.

Aufgabe der Kinetik ist es, alle drei Verseifungskonstanten zahlenmäßig, wenigstens der Größenordnung nach, zu ermitteln. Relativ hohe Werte der einen oder der anderen der drei Konstanten werden leicht zu messen, beziehungsweise, wenn die betreffende Reaktion unmeßbar rasch, leicht festzustellen sein. Anders steht es mit den relativ kleinen Werten.

Soll eine kleine Konstante der Wasserverseifung gemessen werden, so wird man die Bedingung der Minimumgeschwindigkeit herbeiführen. Alsdann wird k_w noch zu messen sein, wenn es von derselben Größenordnung ist wie $2k_m$ [siehe Gleichung (15)]. Wenn $k_w \ll 2k_m$, so besteht keine Aussicht, seinen Wert feststellen zu können.

Zwecks Messung eines relativ kleinen k_a oder k_s wird man sich den Bedingungen der Maximalgeschwindigkeiten nähern. Der Fall, daß man beispielsweise k_s in stark saurer Lösung darum nicht messen kann, weil selbst unter dieser Bedingung $k_s[H^+]$ klein gegenüber $k_a[OH^-]$ ist, ist nach den bisherigen Erfahrungen, die bezüglich der Größenordnung der Konstanten gemacht worden sind, kaum zu erwarten. Nach diesen Erfahrungen ist der Bereich der Verseifungskonstanten, wenn an sich groß, so doch wesentlich kleiner als der der realisierbaren Aziditäten von rund 14 Zehnerpotenzen. Man wird also im äußersten Falle Stillstand der Verseifung und damit die Unmeßbarkeit von k_s infolge seiner Kleinheit feststellen können.

Dagegen kommt es vor, daß man sich über die Größenordnung beispielsweise von k_s darum keine Vorstellung verschaffen kann, weil selbst in stark saurer Lösung $k_s[H^+]$ klein gegenüber k_w ist. Alsdann gelingt es mitunter durch Zugabe eines inerten Lösungsmittels das Verhältnis $k_s[H^+] : k_w$ zugunsten von $k_s[H^+]$ soweit zu verschieben, um wenigstens die Tatsache des Vorliegens einer sauren Verseifung konstatieren zu können.

Überblicken wir nünmehr die Verseifung unserer drei Stofftypen mit Äthersauerstoffatomen bezüglich der absoluten und relativen Werte von k_a , k_s und k_w ; so ist auf Grund bisheriger Beobachtungen und Messungen folgendes festzustellen.

Carbonsäureester. Die Konstante der alkalischen Verseifung ist sehr groß und bei den einzelnen Estern sehr verschieden. Beispielsweise ist sie für das erste Methyl des Oxalsäureesters von der Größenordnung 10^6 , für eine große Zahl anderer Methyl ester von der Größenordnung 1 und darunter.

Literatur bei A. Skrabal und A. Matievic: Monatshefte für Chemie, 39 (1918), 765; A. Skrabal und E. Singer, ibid., 44 (1920), 339.

Die Konstante der sauren Verseifung ist klein, bei den verschiedenen Estern nicht sehr verschieden, von der ungefähren Größenordnung 10^{-3} und darunter.

Das Verseifungsgeschwindigkeitsminimum liegt demnach in der Nähe des Neutralpunktes, aber immer auf der sauren Seite desselben, beispielsweise für Äthylacetat bei $[H^+] = 3 \times 10^{-6}$.

Eine Wasserverseifung ist im allgemeinen nicht festzustellen, womit gesagt ist, daß ein etwaiges k_w unter allen Verhältnissen klein gegenüber $k_a[OH^-]$ oder $k_s[H^+]$ ist. Soweit Messungen im Verseifungsminimum¹ vorliegen, sprechen sie für ein selbst gegenüber $2k_m$ [Gleichung (15)] verschwindend kleines k_w . Es wäre wünschenswert, diese Messungen zu vermehren und insbesondere auch auf Ester mit extremen Verseifungsgeschwindigkeiten auszuweiten.

Alkalische neben saurer Verseifung bei nicht nachweisbarer Wasserverseifung und $k_a > k_s$ bedingen bei den Carbonsäureestern ein scharf ausgeprägtes Verseifungsminimum im Gebiete der schwach sauren Reaktion, wie aus der Kurve II der Figur (Abszisse Azidität, Ordinate Reaktionsgeschwindigkeit für $V=1$, beide in logarithmischer Zählung) am Äthylacetat als Beispiel zu ersehen ist.

Die hier dargelegten Beziehungen zwischen den drei Konstanten gelten nur als Regel für die Carbonsäureester. Bei Sulfonsäureestern und Mineralsäureestern liegen die Verhältnisse wesentlich anders.²

Aber auch bei den Carbonsäureestern gibt es bemerkenswerte Abweichungen von der Regel. So haben H. Johansson und H. Sebelius³ bei der Hydrolyse des Glykolids zu Glykologykolsäure und des Lactids zu Lactomilchsäure neben einer unmeßbar raschen alkalischen Verseifung⁴ und einer meßbaren sauren Verseifung eine meßbare Wasserverseifung feststellen können. Es liegt also hier der Fall einer Carbonsäureesterverseifung vor, bei welcher k_w gegenüber $[H^+]k_s$ nicht mehr zu vernachlässigen ist.

Was die Lactone anbelangt, so verhalten sich die γ -Lactone normal, d. h. wie die Mehrzahl der übrigen Carbonsäureester. Was hingegen die β -Lactone betrifft, so konnten dieselben Forscher⁵

¹ J. J. A. Wijs, Zeitschr. f. physik. Chemie, 11 (1893), 492, und 12 (1893), 514; H. v. Euler und J. Laurin, Arkiv för Kemi, Mineralogi och Geologi, 7 (1920), Nr. 30.

² Literatur bei R. Wegscheider, Ber. chem. Ges., 52 (1919), 235.

³ Ber. chem. Ges., 52 (1919), 745.

⁴ Es ist uns inzwischen gelungen, auch diese rasche Reaktion zu messen, so daß nunmehr in dem Lactid ein Ester vorliegt, von welchem alle drei Konstanten k_a , k_s und k_w dem Zahlenwerte nach bekannt sind. Wir werden über unsere Messungen in Bälde berichten.

⁵ Ber. chem. Ges., 51 (1918), 480.

besonders extreme Abweichungen vom normalen Verhalten aufzeigen, insofern die Hydrolyse der β -Lactone durch Wasserstoffion nicht (oder wenig) katalysiert wird.

Hinsichtlich der geltenden Beziehung $k_n \gg [H^+]k_s$, erinnern die β -Lactone bereits an die Säureanhydride.

Carbonsäureanhydride. Die Verseifung oder Hydratisierung der Carbonsäureanhydride¹ ist durch einen hohen Wert der Konstante der Wasserverseifung gekennzeichnet. Beispielsweise ist für Acetanhydrid bei 25° $k_n = 0.17$, entsprechend einer Halbierungszeit von rund 4 Minuten. Gegenüber diesem Betrag kommt $[H^+]k_s$ schwer zur Geltung und die Behauptung von A. C. D. Rivett und N. V. Sidgwick,² daß Wasserstoffion die Hydratisierung der Säureanhydride nicht beschleunigt, ist leicht verständlich. Dem hingegen haben K. J. P. Orton und M. Jones³ feststellen können, daß auch diese Hydrolyse durch Wasserstoffion beschleunigt wird, wenn auch nicht so augenscheinlich wie die Esterverseifung. Die beiden Forscher haben ferner gezeigt, daß die Säuren namentlich in wasserarmen Medien sehr wirksame Katalysatoren sind. Neben der Wasserverseifung ist also die saure Verseifung der Anhydride feststehend.

Die Beschleunigung der Hydratisierung der Anhydride durch Säuren (Salzsäure, Schwefelsäure) geht übrigens ganz zweifellos auch aus älteren Beobachtungen mehr qualitativer Natur hervor.⁴

Hydroxylion ist ein außerordentlich wirksamer Katalysator für die Hydratisierungsreaktion.⁵ Die Konstante der alkalischen Verseifung konnte bisher noch nicht ermittelt werden.⁵ Die Schwierigkeiten liegen weniger an dem hohen Wert von k_a als an der Größe von k_n , sind also ähnlicher Art wie die, die sich der Ermittlung von k_s entgegenstellen. Weil die Verseifung in mittelstarksaurer Lösung eine reine Wasserverseifung ist, muß in diesen Lösungen $[OH^-]k_a$ klein gegen k_n sein. Es wäre daher ein Leichtes, $[H^+]$ derart zu verringern, daß $[OH^-]k_a$ gegen k_n groß ist, alsdann ist aber, weil k_n an sich einen hohen Wert hat, $[OH^-]k_a + k_n$ um so größer und damit die Reaktion an die Grenze der Meßbarkeit gelangt. Mit diesen Schwierigkeiten hat man also bei der Messung von k_a zu rechnen. Immerhin läßt sich schon heute sagen, daß das k_a langsam alkalisch verseifender Anhydride ungefähr ebenso groß ist wie das k_a rasch alkalisch verseifender

¹ Siehe insbesondere die Arbeiten von P. E. Verkade in den Rec. trav. chim.

² Journ. Chem. Soc., 97 (1910), 732 und 1677. Vgl. auch B. H. Wilsdon und N. V. Sidgwick, ibid., 103 (1913), 1959.

³ Journ. Chem. Soc., 101 (1912), 1708.

⁴ Vgl. u. a. J. Volhard, Liec. Ann., 267 (1892), 51; R. Wegscheider und E. Späth, Monatshefte für Chemie, 30 (1909), 841.

⁵ Über eine Schätzung von k_a beim Kampfersäureanhydrid siehe B. H. Wilsdon und N. V. Sidgwick, Journ. Chem. Soc., 102 (1915), 679.

Ester.¹ Es ist also die Reaktionsfähigkeit eines Acyls A bezüglich der alkalischen Verseifung in dem Anhydrid AOA' im allgemeinen größer als in dem Ester AOR , so daß die Anhydride durchschnittlich rascher alkalisch verseifen als die Ester.

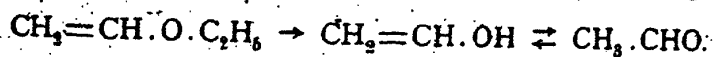
Nach dem Gesagten hat die Verseifungskurve der Carbonsäureanhydride ungefähr den Verlauf der Kurve III unserer Figur. Weil das Verhältnis $k_p : k_s$ einen größeren Wert hat als bei den Estern, ist das Verseifungsminimum stärker nach der sauren Seite verschoben und infolge der Relation $k_v \gg 2k_m$ überdies ganz eingeebnet.

Äther. Gegenüber den Estern und noch mehr gegenüber den Carbonsäureanhydriden sind die Äther sehr häufig, aber nicht immer durch große Reaktionsträgheit gekennzeichnet. Dieses geringe Reaktionsvermögen kommt auch in ihrem Verhalten im Hydratations- oder Verseifungsvorgang zum Ausdruck. Mit Wasser reagieren viele Äther nur sehr langsam zu Alkohol und diese langsame Reaktion ist sehr wahrscheinlich eine saure Verseifung.

Die ältesten hierhergehörigen Beobachtungen am Äthyläther verdanken wir A. Lieben.² Reiner Äther zeigt bei Gegenwart von Wasser nach einigen Monaten, rascher bei 100° im Einschmelzrohr, Jodoformreaktion infolge Alkoholbildung. Der Umstand, daß basische Körper, wie Kalk und Ätzkali, den Äther nach Lieben nicht angreifen, während Säuren und Salze ihn verändern, spricht mit einiger Wahrscheinlichkeit dafür, daß auch die Reaktion mit Wasser keine reine Wasserverseifung, sondern eine saure, durch das Wasserstoffion des Wassers bedingte Verseifung ist. Es ist also immer $[H']k_s > k_v$.

Daß die Hydrolyse der Äther eine saure Verseifung ist, folgt aus zahlreichen Beobachtungen an rascher hydrolysierenden Äthern und aus einigen Messungen. Der Wert der Konstanten k_s ist sehr von der Natur des Alkyls abhängig. Nach A. Eltekoff³ verseifen die Äther tertiärer Alkohole rascher als die Äther sekundärer Alkohole, letztere wieder rascher als die Äther primärer Alkohole, die Äther ungesättigter Alkohole verseifen rascher als die Äther gesättigter Alkohole.

Besonders rasch hydrolysieren unter dem Einfluß von Säuren, beziehungsweise des Wasserstoffions die Enoläther.⁴ So wird Vinyläthyläther nach J. Wislicenus⁵ durch Eintropfenlassen in verdünnte Schwefelsäure glatt in Alkohol und Aldehyd gespalten:



¹ Ich hoffe über die alkalische Verseifung der Anhydride, wenigstens was die Größenordnung von k_a anbelangt, demnächst berichten zu können. (A. S.).

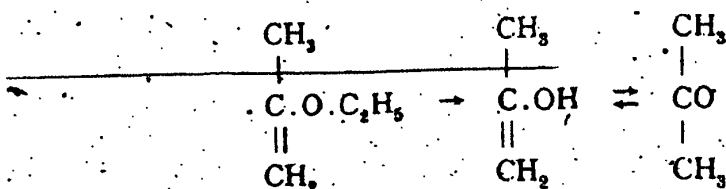
² Lieb. Ann., 165 (1873), 134.

³ Ber. chem. Ges., 10 (1877), 704 und 1902.

⁴ L. Knorr, Ber. chem. Ges., 39 (1906), 1409.

⁵ Lieb. Ann., 192 (1878), 119.

Nach A. Faworsky¹ wird Isopropenyläthyläther schon durch 1%ige-Schwefelsäure rasch und in der Kälte vollständig in Alkohol und Aceton zerlegt:



Ebenso wie die Äther tertiärer Alkohole rascher hydrolysieren als die Äther sekundärer Alkohole, scheinen auch die Äther tertiärer Enole rascher zu reagieren als die Äther der Enole, deren Hydroxyl sekundär gebunden ist.

Die größere Hydrolysegeschwindigkeit der Enoläther gegenüber der geringeren der Äther ungesättigter Alkohole entspricht dem viel größeren Einfluß der α -Substitution gegenüber dem der β -Substitution.

Im Gegensatz zu den rasch hydrolysierenden Äthern der tertiären Enole sind die Phenoläther durch große Beständigkeit gekennzeichnet, ein Zeichen, daß nicht allein die Art der Bindung der Alkoholgruppe, sondern die gesamte Kernstruktur des Alkyls für die Reaktionsgeschwindigkeit bestimmend ist.

Äthernatur besitzen ferner die Aldehyd- und Ketonacetale.² Sie werden bei Gegenwart von Säuren rasch zu Alkohol und Aldehyd, beziehungsweise Keton hydrolysiert.³ Auch hier scheinen die Acetale der Ketone leichter zu reagieren als die der Aldehyde.⁴

Im Anschluß an die Acetale wären die Polysaccharide und Glykoside namhaft zu machen. Ihre Hydrolyse, wie die vieluntersuchte Rohrzuckerinversion, oder die Spaltung des Salicins⁵ in Dextrose und Saligenin, sind saure Verseifungen, indem die Hydrolysegeschwindigkeit der Wasserstoffionkonzentration proportional ist.

Gewissermaßen potenziert erscheint der Äthercharakter in den Orthocarbonsäureäthern, die drei Alkoxygruppen an dasselbe Kohlenstoffatom gebunden haben. Die saure Verseifung erfolgt hier, wie wir für einen Fall zeigen konnten, auch in neutraler Lösung mit großer, ja selbst noch in schwach alkalischer Lösung mit merklicher Geschwindigkeit.

¹ Journ. prakt. Chemie, [2], 37 (1888), 534.

² Mit der Messung der Hydrolyse der Acetale sowie der Acylderivate der gem. Glykole, welche letztere natürlich Esternatur besitzen, sind wir derzeit beschäftigt. (A. S.)

³ M. Dalepine, Compt. rend., 132 (1901), 331. Vgl. auch M. Grödzki, Ber. chem. Ges., 16 (1883), 512.

⁴ L. Claisen, Ber. chem. Ges., 40 (1907), 3903.

⁵ A. A. Noyes und W. J. Hall, Zeitschr. physik. Chemie, 18 (1895), 240.

Die Bezeichnung der alkylierten Orthocarbonsäuren als Ester ist somit nicht gerechtfertigt. Auch die hypothetischen Muttersubstanzen tragen ihren Namen mit Unrecht, sie wären sachgemäßer als Geminalglyoerine zu bezeichnen; das erste Glied HC(OH)_2 sollte, also Methenylglycerin heißen.¹

Stellt man den Wert 70000 für Methenylglycerinäthyläther, 0.01 für die Rohrzuckerinversion² und den sicher sehr kleinen Wert der bisher noch nicht quantitativ gemessenen sauren Äthylätherhydrolyse in eine Parallele, so erhält man eine Vorstellung von dem Bereich, innerhalb welchen das k_s der Ätherverseifung sich bewegen kann.

Dieser Bereich steht an Umfang sicherlich nicht nach dem Bereich von k_a bei der Esterverseifung und ist mutmaßlich ebenso umfassend wie der Bereich von k_a der Anhydridverseifung.

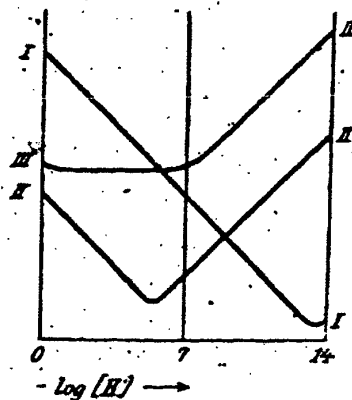
Die reaktionsfähigen Äther sind durch ein großes k_s ebenso gekennzeichnet, wie die reaktionsfähigsten Anhydride durch ein großes k_a . Die Ester halten die Mitte, ihre reaktiven Vertreter haben hohe Werte von k_s und k_a , die aber, an den Werten von k_s , beziehungsweise k_a der reaktiven Äther, beziehungsweise Anhydride gemessen, mutmaßlich zurückbleiben.

Mit der Verseifungsgeschwindigkeit symbar verläuft die allgemeine Reaktionsfähigkeit der Äther, Ester und Anhydride. Die rasch verseifenden Vertreter dieser Stoffklassen sind daher auch die wirksamsten Alkylierungs-, beziehungsweise Acylierungsmittel. Man macht von ihnen in der Synthese Gebrauch. Die langsam verseifenden sind hingegen als inerte Lösungsmittel von praktischer Bedeutung.

Nach den numerischen Werten der Verseifungskonstanten kommen für diesen Zweck vor allem die Äther gesättigter, primärer Alkohole in Betracht.

Was k_a und k_w der Ätherverseifung anbelangt, so sind, soweit Messungen vorliegen, Anzeichen für eine merkliche Wasserverseifung nicht vorhanden. Ähnlich wie bei den Estern, dürfte also auch bei den Äthern k_w klein gegenüber $[\text{H}^+]k_s$ sein.

Dagegen liegen zuweilen Anzeichen einer alkalischen Verseifung vor, wenn auch die Gebiete, wo Äther vorwiegend alkalisch verseifen, kaum mehr in den Bereich wässriger Lösungen fallen.



¹ Vgl. auch W. Lippert, Lieb. Ann., 276 (1893), 176.

² W. Ostwald, Journ. prakt. Chemie, 29 [2], (1884), 385.

So werden die Phenoläther bei längerem Erhitzen mit alkoholischem Alkali oder durch die Alkalischmelze gespalten.¹ Äther mehrwertiger Phenole werden dabei, ganz so wie die Ester mehrwertiger Carbonsäuren, partiell oder stufenweise verseift.²

Jedenfalls ist das k_a bei den typischen Äthern sehr klein gegenüber dem k_s , so daß das Verseifungsminimum im stark alkalischen Gebiete liegen und mitunter gar nicht realisierbar sein dürfte. Aus Stetigkeitsgründen wird man aber auf ein Verseifungsminimum schließen dürfen.

Die Kurve I der Figur zeigt den Verlauf der Verseifungskurve der Äther, wie wir ihn auf Grund unserer bisherigen Erfahrungen als typisch für diese Stoffklasse anzunehmen einigermaßen berechtigt sind.

Ordnen wir sonach die drei Stofftypen mit Äthersauerstoffatom in die Reihe:

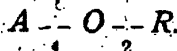
Äther, Ester, Anhydride,

so nehmen in derselben Reihenfolge die numerischen Werte von k_a und des Verhältnisses $k_a : k_s$ zu, während sich das Verseifungsminimum aus dem Gebiete der stark alkalischen Reaktion in das Gebiet der sauren Reaktion verschiebt und gleichzeitig immer mehr abflacht.

Daß hier alle Abstufungen aufzutreten vermögen, wurde schon betont. So vermitteln die Phenoläther den Übergang von den Äthern zu den langsam verseifenden Estern, die Lactide und β -Lactone den Übergang von den Estern zu den Carbonsäureanhydriden. Derartige Übergänge werden sich bei weiterem Studium des Verseifungsphänomens noch vielfach auffinden lassen.

Von den drei Stofftypen sind die Ester am besten untersucht und demgemäß ist auch die Theorie der Esterverseifung³ bisher am weitesten gediehen. Jeder neue Standpunkt wird auf dieses vielerörterte Problem auch neues Licht zu werfen vermögen. Es fragt sich, ob dies nicht auch für den von Verkade und im Vorliegenden auch von uns eingenommenen Standpunkt der Analogie der drei Stofftypen mit Äthersauerstoffatom zutrifft.

Wie schon van't Hoff⁴ dargetan hat, besitzt der Ester AOR zwei Stellen im Molekül, an welchen der Angriff der verseifenden Agentien (Wasser, Säure, Base) stattfinden kann:



¹ R. Stoermer und B. Kahlert, Ber. chem. Ges., 34 (1901), 1812.

² L. Bouveault, Bull. Soc. Chim., [3], 19 (1898), 75.

³ Hinweise auf zusammenfassende Darstellungen dieser Theorien finden sich bei H. Johansson und H. Sebelius, Ber. chem. Ges., 52 (1919), 747, Fußnote 3.

⁴ J. H. van't Hoff, Vorlesungen über theoret. und physik. Chemie, 2. Aufl., 3. Heft (Braunschweig 1903), p. 139.

Er vermutet, daß bei der Verseifung durch Alkali der Angriff an der Stelle 2, bei der Verseifung durch Säuren an der Stelle 1 erfolgt, und stützt seine Vermutung auf den damaligen Stand der Untersuchungen, wonach die Geschwindigkeit bei der alkalischen Verseifung in erster Linie von der Natur des Alkyls, bei der sauren von der Natur des Acyls bestimmt werden soll.

Das Material, das van't Hoff vorgelegen ist, ist ganz unzulänglich. Man braucht sich nur die Werte von k_2 für die Methylester der Ameisensäure, Essigsäure, Benzoesäure, Oxaminsäure,¹ Oxalsäure, Malonsäure, Sebacinsäure etc. vor Augen zu halten, um sofort zu ersehen, wie ungeheuer groß der Einfluß des Acyls bei der Verseifung mit Basen ist. Damit fällt die Vermutung van't Hoff's in sich zusammen.

Aus der Tatsache, wonach k_2 gegenüber k_1 bei den Säureanhydriden, die nur die Stelle 1 haben, sehr groß, bei den Äthern, die nur die Stelle 2 aufweisen, verschwindend klein ist, wäre viel eher zu schließen, daß bei der Esterverseifung durch Alkali der Angriff an der Stelle 1, durch Säuren an der Stelle 2 erfolgt. Also gerade das Gegenteil der van't Hoff'schen Hypothese.

Man wird aber richtiger gehen, wenn man sich wieder der Auffassung anschließt, wonach jede mögliche Reaktion auch tatsächlich stattfindet. Dann wird man annehmen müssen, daß bei allen drei Arten der Esterverseifung (alkalische, saure und Wasserverseifung) der Angriff an beiden Stellen 1 und 2 erfolgt, denn die Anhydride, die nur die Stelle 1 haben, gehen de facto, die Äther, die nur die Stelle 2 haben, wenigstens grundsätzlich alle drei Verseifungswege.

§ Für die Ester — und analog für die »Mischäther«² und »Mischanhydride«³ — gelten dann Überlegungen, die man allgemein für Stoffe mit zwei reaktionsfähigen Gruppen machen kann und in ähnlicher Weise auch wiederholt gemacht hat. Die Verseifung des Esters AOR erfolgt hiernach nach den zwei Nebenreaktionen oder — weil letztere identisch und nur in bezug auf ihren »Reaktionsmechanismus« verschieden sind — nach den zwei »Quasinebenreaktionen«:³



¹ Die Veröffentlichung einer Untersuchung über die Oxaminsäureesterverseifung erfolgt ungefähr gleichzeitig. (A. S.)

² Diese Bezeichnungsweise erscheint uns nicht nur kürzer, sondern auch sachgemäßer als die übliche: »gemischte Äther« und »gemischte Anhydride«.

³ Ist die Ungleichheit der beiden Hälften des Moleküls nicht wie hier auf die beiden Liganden, sondern auf die Unsymmetrie des Kerns zurückzuführen, ist also der Stoff mit den ungleichen Hälften von der Formel $X-AB-X$, so verlaufen wirkliche Nebenreaktionen mit Folgewirkungen.

Bedeutet x_1 den Umsatz und k_a, k'_s, k''_w die drei Konstanten der ersten Reaktion, x_2, k'_a, k'_s, k''_w die entsprechenden Größen der zweiten Reaktion, so gilt für die allein-meßbare Summengeschwindigkeit:

$$\frac{dx}{dt} = \frac{d(x_1 + x_2)}{dt} = (k_a + k'_a)[OH'](a - x) + (k'_s + k'_s)[H'](a - x) + (k''_w + k''_w)(a - x), \quad (17)$$

wenn a die Anfangskonzentration des Esters ist.

Ein Vergleich mit Gleichung (11) ergibt für die Konstanten k_a, k_s, k_w der Verseifung des Esters AOR die Beziehungen:

$$\left. \begin{aligned} k_a &= k'_a + k''_a \\ k_s &= k'_s + k''_s \\ k_w &= k'_w + k''_w \end{aligned} \right\} \quad (18)$$

Sind die beiden, an das Äthersauerstoffatom gebundenen, reaktionsfähigen Gruppen identisch, liegt also ein »Reinäther« ROR oder ein »Reinanhydrid« AOA vor, so ist notwendig $k_a = k'_a$ usw. und demgemäß

$$\begin{aligned} k_a &= 2k'_a = 2k''_a, \\ k_s &= 2k'_s = 2k''_s, \\ k_w &= 2k'_w = 2k''_w. \end{aligned}$$

Es bedeuten dann $0.5 k_a, 0.5 k_s, 0.5 k_w$ die Geschwindigkeiten, mit welchen eine bestimmte Gruppe aus dem Reinäther oder dem Reinanhydrid verseift, oder die »Gruppengeschwindigkeiten«. Sie sind natürlich halb so groß wie die Geschwindigkeiten k_a, k_s, k_w , mit welchen die eine oder die andere der identischen Gruppen reagiert.

Bei Reinäthern und Reinanhydriden sind mit den experimentell ermittelbaren Konstanten k_a, k_s, k_w also auch die Gruppenkonstanten $k'_a = k'_a = 0.5 k_a$ usw. gegeben, bei Mischoxyden bleiben sie unbekannt.

Es fragt sich nun, ob man aus den Konstanten der beiden Reinoxide XOX und $X'OX'$ auf die Konstanten des Mischoxydes XOX' zu schließen vermag.

Dies ist ohneweiters in dem Grenzfall möglich, daß die reaktionsfähigen Gruppen unbeeinflusst und unabhängig voneinander reagieren. Wenn also das X mit derselben Gruppengeschwindigkeit aus dem XOX wie aus dem XOX' , und das X' mit derselben Gruppengeschwindigkeit aus dem $X'OX'$ wie aus dem XOX' herausverseift, dann ist

$$\left. \begin{aligned} k_a &= 0.5(p_a + q_a), \\ k_s &= 0.5(p_s + q_s), \\ k_w &= 0.5(p_w + q_w), \end{aligned} \right\} \quad (19)$$

wö die indizierten k die Konstanten des Mischoxydes und p und q die der beiden Reinoxyde bezeichnen.

Die Gleichungen (19) besagen, daß die Geschwindigkeit gleich der Summe der Gruppengeschwindigkeiten oder daß die Geschwindigkeit des Mischoxydes gleich dem arithmetischen Mittel aus den Geschwindigkeiten der beiden Reinoxyde ist.

Prüft man die Gleichungen (19) an der Hand der Messungen, so zeigt sich, daß sie in der Wirklichkeit nicht erfüllt sind. Nehmen wir Äthylacetat als Beispiel, so würden die k die Verseifungskonstanten dieses Esters, die p die Konstanten des Essigsäureanhydrids, die q die Konstanten des Äthyläthers bedeuten. Von den Konstanten der beiden Reinoxyde ist zwar nur die Wasserkonstante des Anhydrids dem Werte nach bekannt, doch weiß man mit Sicherheit, daß q_a gegenüber p_a und q_w gegenüber p_w , und sehr wahrscheinlich auch q_s gegenüber p_s verschwindend klein ist. Hieraus und aus (19) würde folgen, daß auf allen drei Verseifungswegen das Äthylacetat halb so rasch reagieren sollte als das Acetanhydrid. Nicht nur bloß, daß dies bei weitem nicht zutrifft, auch die wechselseitigen Verhältnisse der drei Verseifungskonstanten sind bei dem Ester ganz andere als bei dem Anhydrid, wie weiter oben gezeigt worden ist.

Nun sind Acetyl und Äthyl zwei fern voneinander abliegende Gruppen und es ist vielleicht von vornherein zu gewärtigen, daß die Gleichungen (19) zugrundeliegende Bedingung um so besser erfüllt ist, je ähnlicher sich in chemischer Hinsicht die beiden an den Brückensauerstoff gebundenen Gruppen verhalten. Als einen derartigen Fall können wir das von P. E. Verkade¹ gemessene Mischanhydrid der Essigsäure und Propionsäure heranziehen. Für 25° sind die Konstanten der Wasserverseifung der drei Stoffe die folgenden:

Acetyloxyd	Propionyloxyd	Mischanhydrid
0.1641	0.0857	0.1206

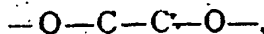
Auch in diesem denkbar günstigsten Falle ist Gleichung (19) nur ganz ungefähr erfüllt:

$$0.5(0.1641 + 0.0857) = 0.1249 \sim 0.1206.$$

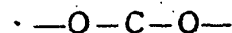
Die beiden an den Brückensauerstoff —O— gebundenen Gruppen reagieren somit nicht unabhängig voneinander, sie beeinflussen sich gegenseitig.

¹ Rec. trav. chim., 35 (1915), 79 und 299.

Das war nach den bei den Estern zweibasischer Säuren und zweisäuriger Alkohole gemachten bisherigen Erfahrungen ziemlich vorauszusehen. Nach diesen Erfahrungen ist die Bedingung der unbeeinflussten Reaktion zweier Gruppen um so besser erfüllt, je länger die Atomkette ist, die die beiden reaktionsfähigen Gruppen miteinander verbindet. Die kürzeste Kette, die in drei Fällen (saure Verseifung der Oxalsäureester, saure und alkalische Verseifung der Äthylenglykolester) noch unbeeinflusste Reaktion der Liganden zeigte, war die Kette



während bereits die Kette (Fall der Kohlensäureester und des Ortho-ameisensäureäthers)



außerordentlich starke gegenseitige Beeinflussung der Liganden ergab. Um so mehr ist letztere für die Kette $X-O-$ zu erwarten.

An Stelle der Gleichungen (19) haben daher Gleichungen der Form

$$k = 0.5(pf + qg) \quad (20)$$

zu treten, wo f und g Faktoren sind, die die gegenseitige Beeinflussung der Gruppen X und X' in XOX' zahlenmäßig zum Ausdruck bringen. Die Faktoren müssen derart beschaffen sein, daß sie sich in dem Maße dem Werte Eins nähern, als X und X' der Identität nahekommen, so daß für $X' = X$ auch $f = g = 1$ wird, in welchem Grenzfalle (20) in (19) übergeht.

An das Aufsuchen entsprechender Funktionen für f und g wird man schreiten können, wenn die drei Konstanten einer größeren Zahl von Reinäthern und Reinanhydriden sowie der entsprechenden Mischoxyde einmal bekannt sein werden. Einstweilen liegt nur ein einziger Fall vor, wo ein Probieren möglich ist: die schon erwähnte Wasserverseifung des Essigsäure-Propionsäureanhydrids. Hier läßt sich (20) in die Form¹ bringen:

$$k_w = 0.5 \left(p_w \sqrt{\frac{\delta_2}{\delta_1}} + q_w \sqrt{\frac{\delta_1}{\delta_2}} \right),$$

wo δ_1 die Dissoziationskonstante der Säure des Reinanhydrids mit der Verseifungskonstante p_w ist und δ_2 die analoge Bedeutung hat.

Setzt man $\delta_1 = 1.82 \times 10^{-5}$ und $\delta_2 = 1.31 \times 10^{-5}$, so wird

$$k_w = 0.5(0.1641 \times 0.8484 + 0.0857 \times 1.1787) = 0.1201,$$

also innerhalb der Fehler identisch mit dem experimentell gefundenen Wert $k_w = 0.1206$.

¹ Diese Form steht in naher Beziehung zu den »reduzierten Hydratationskonstanten« von Verkade.

Weil Essigsäure und Propionsäure chemisch sehr nahestehend sind, vermag diese Übereinstimmung vorläufig noch nicht viel zu besagen.

Aufgabe der chemischen Kinetik muß es sein, aus möglichst wenig Naturkonstanten die Geschwindigkeit der Verseifung aller Ester vorauszuberechnen. Hält man sich vor Augen, daß, wie vor kurzem¹ gezeigt werden konnte, neben der chemischen Natur der reagierenden Stoffe auch ihre Konzentration für den Grad der Unabhängigkeit der reagierenden Gruppen maßgebend ist, daß die »Konstanten« der Reaktionsgeschwindigkeit nur über geringe Bereiche annähernd konstant sind, so wird man nicht umhin können, E. Färber² recht zu geben, welcher den Ausspruch getan: »Jede Erklärung, auch die einer chemischen Reaktion, ist eine unendliche Aufgabe.«

Die Verseifung des Ameisensäureäthylesters.

Auf die Hydrolyse des Methenylglycerinäthyläthers zu Ameisensäureester:



folgt die Verseifung des letzteren zu Ameisensäure:



Während die erste Reaktion mit merklicher Geschwindigkeit nur unter dem katalytischen Einfluß des Wasserstoffions erfolgt und also eine typische Ätherverseifung ist, wird die zweite Reaktion ebensowohl durch Wasserstoffion, wie Hydroxylion katalysiert, gehört also zur Klasse der Esterverseifungen.

Demgemäß gibt es eine saure und eine alkalische Verseifungskonstante der Reaktion (2). Die erstere wurde im vorhergehenden zu

$$k_s = 0.192$$

ermittelt. Die Konstante der alkalischen Verseifung wurde bisher nach zwei elektrochemischen Methoden und rein chemisch mit Hilfe einer Jodid-Jodat-Lösung als Wasserstoffionpuffer gemessen.

In letzterer Lösung verläuft die Reaktion langsamer als erwünscht. In einer Ammoniak-Ammonsalzlösung ist die Geschwindigkeit bequem meßbar, doch bestehen dieser Methode gegenüber Bedenken, da Nebenreaktionen unter Amidbildung nicht unwahrscheinlich sind. Die noch stärker alkalische Reaktion des Carbonat-

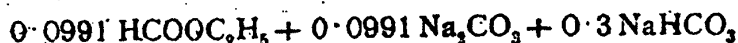
¹Vgl. A. Skrabal und E. Singer, Monatshefte für Chemie, 47 (1920), 339.

²Die Naturwissenschaften, 8 (1920), 322.

Bicarbonatpuffers ermöglicht die Meßbarkeit nur bei großem Bicarbonatzusatz. Unter diesen Verhältnissen sind jene Übelstände in Kauf zu nehmen, auf welche schon ausführlich verwiesen wurde. Trotzdem erschien es mit Rücksicht darauf, daß bessere Methoden zurzeit nicht bekannt sind, angezeigt, die Reaktion auch auf diesem Wege zu messen.

Die Durchführung und Berechnung des Versuches geschah in derselben Weise wie seinerzeit.¹

Versuch 12.



t	$\alpha-x$	k
0	0.0592	—
8	0.0508	0.17
21	0.0362	0.19
46	0.0282	0.16
215	0.0080	0.19
		Mittel... 0.18

Unter Benutzung von 6×10^{-11} für die zweite Dissoziationskonstante der Kohlensäure berechnet sich für $[\text{OH}^-] = 1$:

$$k_a = 1080,$$

ein Wert, der mit dem in der Jodid-Jodatlösung gefundenen genügend übereinstimmt, wenn man bedenkt, daß die Aziditäten, bei welchen hier und dort gearbeitet wurde, um drei Zehnerpotenzen auseinanderliegen.

Der hohe Wert von k_a entspricht der Stärke der Ameisensäure. Die Anschauung, daß ein Ester in der Regel um so rascher verseift, je stärker seine Carbonsäure ist, ist wiederholt geäußert worden und im großen ganzen durch die Erfahrung so ziemlich bestätigt. Auffallend hingegen ist der hohe Wert k_s der sauren Verseifung. Die Ameisensäureester verseifen sauer 20- bis 30mal rascher als die Essigsäureester und Homologen. Mit der Säurestärke kann das große k_s kaum in Zusammenhang gebracht werden, denn die Ester viel stärkerer Säuren, als Ameisensäure verseifen sauer langsamer als die Ameisensäureester. Der hohe Wert von k_s scheint vielmehr in der chemischen Natur der Ameisensäure begründet zu sein.

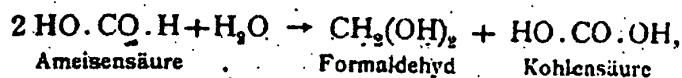
In der Tat ist die Ameisensäure sowohl ihrem Verhalten wie ihrer Formel nach ebensowohl Carbonsäure (Wasserstoffcarbonsäure) wie Aldehyd (Oxyformaldehyd). Für die Aldehydnatur der Ameisensäure spricht ihre leichte Oxydierbarkeit, die ganz im

¹ A. Skrabal und E. Singer, Monatshefte für Chemie, 40 (1919), 383.

Gegensatz steht zur Schwierigkeit, mit welcher Essigsäure zu oxydieren ist, ferner der Umstand, daß sie, ähnlich dem Formaldehyd und gewissen Aldehyden überhaupt:



die Cannizzaro'sche Reaktion zu geben vermag:



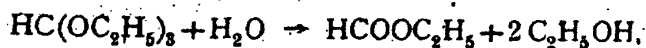
namentlich, wenn einzelne ihrer Salze rasch erhitzt werden, sowie schließlich der weitere Umstand, daß sie sich nach M. Prud'homme¹ auch ihren thermochemischen Daten nach wie ein Gemisch aus Carbonsäure und Aldehydalkohol verhält.

Man wird daher kaum fehlgehen, wenn man die rasche alkalische Verseifung des Äthylformiats auf seine Esternatur (Ameisensäureester), die rasche saure Verseifung auf seine Äthernatur (Äthoxyformaldehyd) zurückführt. Wie im vorstehenden gezeigt wurde, ist die rasche saure Verseifung für die reaktionsfähigen Äther charakteristisch. Als Äther eines sekundären Alkohols und im Hinblick auf die ähnliche Atomgruppierung wie im Methenylglycerinäther, mit welchem er im genetischen Zusammenhang steht, ist die rasche saure Verseifung des Äthoxyformaldehyds nicht verwunderlich.

In dem Äthylformiat haben wir demnach einen Stoff vorliegen, der den Übergang von den Estern zu den reaktionsfähigen Äthern vermittelt, ähnlich wie die Phenoläther den Übergang von den Äthern zu den reaktionsträgen Estern bilden.

Zusammenfassung.

Es wurde die Hydrolysegeschwindigkeit des Orthoameisensäureäthyläthers gemessen. Sie verläuft über Ameisensäureester als faßbare Zwischenstufe:



Die zweite Reaktion ist eine gewöhnliche Esterverseifung. Ihre schon bekannten Konstanten der sauren und alkalischen Verseifung wurden neuerlich gemessen. Für 25° wurde $k_s = 0.192$ und $k_a = 1080$ gefunden.

Was die erste Reaktion anbelangt, so wurde festgestellt, daß sie in alkalischer Lösung unmeßbar langsam vor sich geht. Hieraus folgt, daß das Äthylorthoformiat weder durch Wasser allein noch unter dem Einfluß von Hydroxylon merklich hydrolysiert.

¹ Journ. de chim. physique, 16 (1918), 438.

Hingegen verläuft die Reaktion in stark saurer Lösung unmeßbar rasch. Die Bildung von Ameisensäure aus dem Orthoäther in mineralsaurer Lösung muß daher mit einer Geschwindigkeit erfolgen, die der Geschwindigkeit der sauren Verseifung des Äthylformiats $k_s = 0.192$ gleichkommt. Die Messungen haben dies bestätigt.

Zur Messung der raschen Reaktion erwies sich ein Wasserstoffionpuffer aus primärem und sekundärem Phosphat geeignet. Zur Ermittlung des Reaktionsfortschrittes wurde der gebildete Ameisensäureester durch Analyse bestimmt. Letzterer reagiert bei der Azidität des Phosphatpuffers und während der Dauer der Versuche zu einem nur sehr geringen Ausmaß. Damit war der Vorgang der Hydrolyse des Orthoäthers zu Ameisenester isoliert und gleichzeitig sein Verlauf in einem Medium konstanter Azidität erreicht. Die Messungen ergaben eine Reaktion erster Ordnung und die Proportionalität zwischen Geschwindigkeit und Wasserstoffionkonzentration. Die auf $[H^+] = 1$ bezogene Geschwindigkeitskonstante hat den im Vergleich mit anderen sauren Verseifungen ungewöhnlich hohen Wert $k = 70000$.

Im Anschluß an diese Experimentalergebnisse und im Zusammenhang mit hierhergehörigen Darlegungen von P. E. Verkade wurde die Verseifung der drei Stofftypen ROR' , AOR , AOA' , wo R Alkyle, A Acyle bedeuten, theoretisch besprochen und die Zugehörigkeit des Äthylorthoformiats zum Äthertypus aufgezeigt.

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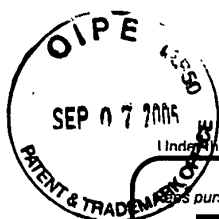
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	Filing Date	06/27/2003	
	First Named Inventor	Nguyen, et al.	
	Art Unit	3672	
	Examiner Name	George A. Suchfield	
Total Number of Pages in This Submission	110	Attorney Docket Number	2002-IP-009210U1

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<input checked="" type="checkbox"/> Extension of Time Request <input type="checkbox"/> Express Abandonment Request <input type="checkbox"/> Information Disclosure Statement	<input type="checkbox"/> Terminal Disclaimer <input type="checkbox"/> Request for Refund <input type="checkbox"/> CD, Number of CD(s) _____ <input type="checkbox"/> Landscape Table on CD	<input type="checkbox"/> Proprietary Information <input type="checkbox"/> Status Letter <input checked="" type="checkbox"/> Other Enclosure(s) (please identify below): Original Copy and English Translation Return Postcard
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SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT		
Firm Name	Halliburton Energy Services, Inc.	
Signature		
Printed name	Robert A. Kent	
Date	9-7-2005	Reg. No. 28,626

CERTIFICATE OF TRANSMISSION/MAILING		
I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date shown below:		
Signature		
Typed or printed name	Tammy Knight	Date 9/7/05

This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.



PTO/SB/17 (12-04v2)

Approved for use through 07/31/2006. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Effective on 12/08/2004.

Pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).

FEE TRANSMITTAL
For FY 2005☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT** (\$) 120.00**Complete if Known**

Application Number	10/608,291
Filing Date	06/27/2003
First Named Inventor	Nguyen, et al.
Examiner Name	George A. Suchfield
Art Unit	3672
Attorney Docket No.	2002-IP-009210U1

METHOD OF PAYMENT (check all that apply)

- ☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____
- ☒ Deposit Account Deposit Account Number: 08-0300 Deposit Account Name: Halliburton
- For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)
- ☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee
- ☒ Charge any additional fee(s) or underpayments of fee(s) under 37 CFR 1.16 and 1.17 ☒ Credit any overpayments

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**FEE CALCULATION****1. BASIC FILING, SEARCH, AND EXAMINATION FEES**

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	300	150	500	250	200	100	
Design	200	100	100	50	130	65	
Plant	200	100	300	150	160	80	
Reissue	300	150	500	250	600	300	
Provisional	200	100	0	0	0	0	

2. EXCESS CLAIM FEESFee Description

	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	50	25
Each independent claim over 3 (including Reissues)	200	100
Multiple dependent claims	360	180

<u>Total Claims</u>	<u>Extra Claims</u>	<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>	<u>Multiple Dependent Claims</u>	
- 20 or HP = _____	x _____	= _____		<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>

HP = highest number of total claims paid for, if greater than 20.

<u>Indep. Claims</u>	<u>Extra Claims</u>	<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>
- 3 or HP = _____	x _____	= _____	

HP = highest number of independent claims paid for, if greater than 3.

3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$250 (\$125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

<u>Total Sheets</u>	<u>Extra Sheets</u>	<u>Number of each additional 50 or fraction thereof</u>	<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>
- 100 = _____	/ 50 = _____	(round up to a whole number) x _____	= _____	

4. OTHER FEE(S)

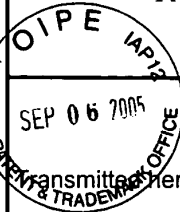
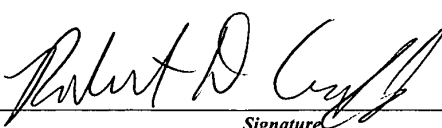



Non-English Specification, \$130 fee (no small entity discount)

Other (e.g., late filing surcharge): One-Month Petition for Extension of Time 120.00**SUBMITTED BY**

Signature	<u>Robert A. Kent</u>	Registration No. (Attorney/Agent)	28,626	Telephone	580-251-3125
Name (Print/Type)	Robert A. Kent	Date	<u>9-7-2005</u>		

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

AMENDMENT TRANSMITTAL LETTER (Large Entity)				Docket No. CC-0675											
Applicant(s): Mark R. Fernald et al.															
Application No. 10/712,818	Filing Date 11-12-03	Examiner Douglas N. Washburn	Customer No.	Group Art Unit 2863	Confirmation No. 8840										
Invention: An Apparatus Having and Array of Clamp on Piezoelectric Film Sensors for Measuring Parameters of a Process Flow within a Pipe															
 COMMISSIONER FOR PATENTS:															
Transmitted herewith is an amendment in the above-identified application. The fee has been calculated and is transmitted as shown below.															
CLAIMS AS AMENDED															
	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST # PREV. PAID FOR	NUMBER EXTRA CLAIMS PRESENT	RATE	ADDITIONAL FEE										
TOTAL CLAIMS	36 -	25 =	11	x \$50.00	\$550.00										
INDEP. CLAIMS	2 -	3 =	0	x \$200.00	\$0.00										
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>					\$0.00										
TOTAL ADDITIONAL FEE FOR THIS AMENDMENT					\$550.00										
<input type="checkbox"/> No additional fee is required for amendment. <input type="checkbox"/> Please charge Deposit Account No. _____ in the amount of _____ <input checked="" type="checkbox"/> A check in the amount of \$550.00 to cover the filing fee is enclosed. <input checked="" type="checkbox"/> The Director is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account 50-0260 <input checked="" type="checkbox"/> Any additional filing fees required under 37 C.F.R. 1.16. <input checked="" type="checkbox"/> Any patent application processing fees under 37 CFR 1.17. <input type="checkbox"/> Payment by credit card. Form PTO-2038.															
WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.															
 _____ Signature			Dated: 06 September 2005												
Robert D. Crawford CiDRA Corporation 50 Barnes Park North Wallingford, CT 06492			<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td colspan="2">I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" [37 CFR 1.8(a)] on</td> </tr> <tr> <td style="text-align: center;">6 September 2005</td> <td></td> </tr> <tr> <td style="text-align: center;">(Date)</td> <td></td> </tr> <tr> <td colspan="2" style="text-align: center;">  _____ Signature of Person Mailing Correspondence </td> </tr> <tr> <td colspan="2" style="text-align: center;"> Robert D. Crawford _____ Typed or Printed Name of Person Mailing Correspondence </td> </tr> </table>			I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" [37 CFR 1.8(a)] on		6 September 2005		(Date)		 _____ Signature of Person Mailing Correspondence		Robert D. Crawford _____ Typed or Printed Name of Person Mailing Correspondence	
I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" [37 CFR 1.8(a)] on															
6 September 2005															
(Date)															
 _____ Signature of Person Mailing Correspondence															
Robert D. Crawford _____ Typed or Printed Name of Person Mailing Correspondence															
cc:															

P11LARGE/REV09



9-8-05

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PTO/SB/21 (09-04)

Approved for use through 07/31/2006. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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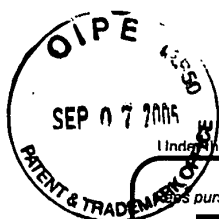
TRANSMITTAL FORM (to be used for all correspondence after initial filing)	Application Number	10/608,291	
	Filing Date	06/27/2003	
	First Named Inventor	Nguyen, et al.	
	Art Unit	3672	
	Examiner Name	George A. Suchfield	
Total Number of Pages in This Submission	110	Attorney Docket Number	2002-IP-009210U1

ENCLOSURES (Check all that apply)		
<input checked="" type="checkbox"/> Fee Transmittal Form <input type="checkbox"/> Fee Attached	<input type="checkbox"/> Drawing(s) <input type="checkbox"/> Licensing-related Papers	<input type="checkbox"/> After Allowance Communication to TC
<input checked="" type="checkbox"/> Amendment/Reply <input type="checkbox"/> After Final <input type="checkbox"/> Affidavits/declaration(s)	<input type="checkbox"/> Petition <input type="checkbox"/> Petition to Convert to a Provisional Application <input type="checkbox"/> Power of Attorney, Revocation Change of Correspondence Address	<input type="checkbox"/> Appeal Communication to Board of Appeals and Interferences <input type="checkbox"/> Appeal Communication to TC (Appeal Notice, Brief, Reply Brief)
<input checked="" type="checkbox"/> Extension of Time Request <input type="checkbox"/> Express Abandonment Request <input type="checkbox"/> Information Disclosure Statement	<input type="checkbox"/> Terminal Disclaimer <input type="checkbox"/> Request for Refund <input type="checkbox"/> CD, Number of CD(s) _____ <input type="checkbox"/> Landscape Table on CD	<input type="checkbox"/> Proprietary Information <input type="checkbox"/> Status Letter <input checked="" type="checkbox"/> Other Enclosure(s) (please identify below): Original Copy and English Translation Return Postcard
<input type="checkbox"/> Certified Copy of Priority Document(s) <input type="checkbox"/> Reply to Missing Parts/ Incomplete Application <input type="checkbox"/> Reply to Missing Parts under 37 CFR 1.52 or 1.53	Remarks	
SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT		
Firm Name	Halliburton Energy Services, Inc.	
Signature		
Printed name	Robert A. Kent	
Date	9-7-2005	Reg. No. 28,626

CERTIFICATE OF TRANSMISSION/MAILING		
I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date shown below:		
Signature		
Typed or printed name	Tammy Knight	Date 9/7/05

This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.



PTO/SB/17 (12-04v2)

Approved for use through 07/31/2006. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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Effective on 12/08/2004.

Pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).

FEE TRANSMITTAL
For FY 2005☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT** (\$) 120.00**Complete if Known**

Application Number	10/608,291
Filing Date	06/27/2003
First Named Inventor	Nguyen, et al.
Examiner Name	George A. Suchfield
Art Unit	3672
Attorney Docket No.	2002-IP-009210U1

METHOD OF PAYMENT (check all that apply)

- ☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____
- ☒ Deposit Account Deposit Account Number: 08-0300 Deposit Account Name: Halliburton
- For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)
- ☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee
- ☒ Charge any additional fee(s) or underpayments of fee(s) under 37 CFR 1.16 and 1.17 ☒ Credit any overpayments

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**FEE CALCULATION****1. BASIC FILING, SEARCH, AND EXAMINATION FEES**

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	300	150	500	250	200	100	
Design	200	100	100	50	130	65	
Plant	200	100	300	150	160	80	
Reissue	300	150	500	250	600	300	
Provisional	200	100	0	0	0	0	

2. EXCESS CLAIM FEESFee Description

	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	50	25
Each independent claim over 3 (including Reissues)	200	100
Multiple dependent claims	360	180

<u>Total Claims</u>	<u>Extra Claims</u>	<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>	<u>Multiple Dependent Claims</u>	
- 20 or HP =	x	=		<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>

HP = highest number of total claims paid for, if greater than 20.

<u>Indep. Claims</u>	<u>Extra Claims</u>	<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>
- 3 or HP =	x	=	

HP = highest number of independent claims paid for, if greater than 3.

3. APPLICATION SIZE FEE

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<u>Total Sheets</u>	<u>Extra Sheets</u>	<u>Number of each additional 50 or fraction thereof</u>	<u>Fee (\$)</u>	<u>Fee Paid (\$)</u>
- 100 =	/ 50 =	(round up to a whole number) x	=	

4. OTHER FEE(S)

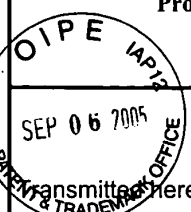
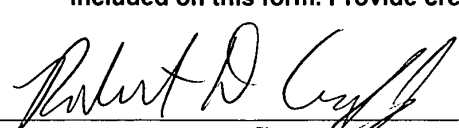
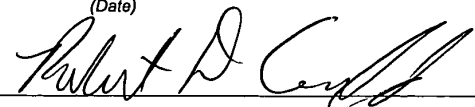
Non-English Specification, \$130 fee (no small entity discount)

Other (e.g., late filing surcharge): One-Month Petition for Extension of Time 120.00**SUBMITTED BY**

Signature		Registration No. (Attorney/Agent) 28,626	Telephone 580-251-3125
Name (Print/Type)	Robert A. Kent	Date	9-7-2005

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

AMENDMENT TRANSMITTAL LETTER (Large Entity)				Docket No. CC-0675	
Applicant(s): Mark R. Fernald et al.					
Application No. 10/712,818	Filing Date 11-12-03	Examiner Douglas N. Washburn	Customer No.	Group Art Unit 2863	Confirmation No. 8840
Invention: An Apparatus Having and Array of Clamp on Piezoelectric Film Sensors for Measuring Parameters of a Process Flow within a Pipe					
 COMMISSIONER FOR PATENTS:					
Transmitted herewith is an amendment in the above-identified application. The fee has been calculated and is transmitted as shown below.					
CLAIMS AS AMENDED					
	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST # PREV. PAID FOR	NUMBER EXTRA CLAIMS PRESENT	RATE	ADDITIONAL FEE
TOTAL CLAIMS	36 -	25 =	11	x \$50.00	\$550.00
INDEP. CLAIMS	2 -	3 =	0	x \$200.00	\$0.00
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>					\$0.00
TOTAL ADDITIONAL FEE FOR THIS AMENDMENT					\$550.00
<input type="checkbox"/> No additional fee is required for amendment. <input type="checkbox"/> Please charge Deposit Account No. _____ in the amount of _____ <input checked="" type="checkbox"/> A check in the amount of \$550.00 to cover the filing fee is enclosed. <input checked="" type="checkbox"/> The Director is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account 50-0260 <input checked="" type="checkbox"/> Any additional filing fees required under 37 C.F.R. 1.16. <input checked="" type="checkbox"/> Any patent application processing fees under 37 CFR 1.17. <input type="checkbox"/> Payment by credit card. Form PTO-2038.					
WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
 _____ Signature			Dated: 06 September 2005		
Robert D. Crawford CiDRA Corporation 50 Barnes Park North Wallingford, CT 06492			<div style="border: 1px solid black; padding: 5px;"> I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" [37 CFR 1.8(a)] on 6 September 2005 (Date)  _____ Signature of Person Mailing Correspondence Robert D. Crawford _____ Typed or Printed Name of Person Mailing Correspondence </div>		
CC:					

P11LARGE/REV09

Practitioner's Docket No. 2002-IP-009210U1

PATENT



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Philip D. Nguyen, et al.

Application No: 10/608,291

Group No.: 3672

Filed: 6/27/2003

Examiner: unknown

For: COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT

PACK PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUBTERRANEAN WELL

Mail Stop Amendment

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
BEFORE MAILING DATE OF EITHER A FINAL ACTION
OR NOTICE OF ALLOWANCE (37 C.F.R. § 1.97(c))**

NOTE: 37 C.F.R. 1.97: "(c) An information disclosure statement shall be considered by the Office if filed after the period specified in paragraph (b) of this section, provided that the information disclosure statement is filed before the mailing date of any of a final action under § 1.113, a notice of allowance under § 1.311, or an action that otherwise closes prosecution in the application, and it is accompanied by one of:

- (1) The statement specified in paragraph (e) of this section; or
- (2) The fee set forth in § 1.17(p)."

NOTE: "If a final action or notice of allowance is mailed in an application and later withdrawn, the application will be considered as not having had a final action or notice of allowance mailed for purposes of considering an information disclosure statement." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*

(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10 *

☒ with sufficient postage as first class mail.

☐ as "Express Mail Post Office to Addressee"

Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Signature

Date: _____

Chasidy Smith

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [8-4]—page 1 of 3)

BEST AVAILABLE COPY

NOTE: 37 C.F.R. § 1.704(d): "A paper containing only an information disclosure statement in compliance with §§ 1.97 and 1.98 will not be considered a failure to engage in reasonable efforts to conclude prosecution (processing or examination) of the application under paragraphs (c)(6), (c)(8), (c)(9), or (c)(10) of this section if it is accompanied by a statement that each item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart application and that this communication was not received by any individual designated in § 1.56(c) more than thirty days prior to the filing of the information disclosure statement. This thirty-day period is not extendable."

NOTE: "If information submitted during the period set forth in 37 C.F.R. 1.97(c) with a certification is used in a new ground of rejection on unamended claims, the next Office action will not be made final since in this situation it is clear that applicant has submitted the information to the office promptly after it has become known and the information is being submitted prior to a final determination on patentability by the Office. However, the information submitted with a certification can be used in a new ground of rejection and the next Office action made final, if the new ground of rejection was necessitated by amendment of the application by applicant. Where the information is submitted during this period with a fee, the examiner may use the information submitted, e.g., printed publication or evidence of public use, and make the next Office action final whether or not the claims have been amended, provided that no other new ground of rejection which was not necessitated by amendment to the claims is introduced by the examiner. See MPEP 706.07(a). If a new ground of rejection is introduced that is neither necessitated by an amendment to the claims nor based on the information submitted with the fee set forth in 37 C.F.R. § 1.17(p), the Office action shall not be made final." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

WARNING: "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1992 (1141 O.G. 63). But see § 103(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(d) and in a request for continued examination (RCE) under § 1.114.

WARNING: No extension of time can be had under 37 C.F.R. 1.136 (a) or (b) for filing an IDS. 37 C.F.R. 1.97(f).

TIME OF TRANSMITTAL OF ACCOMPANYING INFORMATION DISCLOSURE STATEMENT

1. The information disclosure statement transmitted herewith is being filed **after** three months of the filing date of this national application or the date of entry of the national stage as set forth in § 1.491 in an international application or after the mailing date of the first Office action on the merits, whichever event occurred last but **before** the mailing date of either:
 - (1) a final action under § 1.113 or
 - (2) a notice of allowance under § 1.311,whichever occurs first.

STATEMENT OR FEE

2. Accompanying this transmittal is

(check either A or B below)

A. ☐ a statement as specified in 37 C.F.R. § 1.97(e).

OR

B. ☐ the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(c). (\$180.00).

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [6-4]—page 2 of 3)

BEST AVAILABLE COPY

FEE PAYMENT

(complete this item, if applicable)

3. Applicant elects the option to pay the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(c) (\$180.00).

Fee due \$ _____

METHOD OF PAYMENT OF FEE

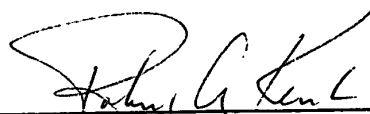
4.

- ☐ Attached is a ☐ check ☐ money order in the amount of \$ _____
- ☐ Authorization is hereby made to charge the amount of \$ _____
- ☒ to Deposit Account No. 08-0300
- ☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

WARNING: Credit card information should not be included on this form as it may become public.

- ☐ Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

A duplicate of this paper is attached.



SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

PO BOX 1431

P.O. Address

DUNCAN OK 73536-0440

Reg. No. 28,626

Tel. No.: (580)-251-3125

Customer No.:

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [8-4]—page 3 of 3)

BEST AVAILABLE COPY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Philip D. Nguyen, et al.

Group No. 3672

Application No.: 10/ 608,291 Examiner:

Filed: 06/27/2003

For COMPOSITIONS AND MEHTODS FOR IMPROVING PROPPANT PACK

PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUB-
COMMERCIAL FOR PRODUCTION TERRANEAN WELL

P.O. Box 1460

Alexandria, VA 22313-1460

STATEMENT FOR INFORMATION DISCLOSURE UNDER
37 C.F.R. § 1.97(c)

NOTE: A statement must state either (1) that each item of information contained in the information disclosure statement was either in a communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement, or (2) that no item of information contained in the information disclosure statement was either in a communication from a foreign patent office in a counterpart foreign application and to the knowledge of the person completing the statement that meeting reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual employed in § 1.97(c) more than three months prior to the filing of the information disclosure statement. 37 C.F.R. § 1.97(c).

Under the first statement under § 1.97(c), it does not matter whether any individual with a duty of disclosure actually knew about any of the information either before receiving the search report. The date on the communication by the foreign patent office begins the 3-month period in the same manner as the mailing of an Office action starts a 3-month shortened statutory period for reply. See § 602.5(a), M.P.E.P., 8th Edition.

DECLARATION UNDER 37 C.F.R. (1) 1.2(a) and 1.10
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, the correspondence is being:

MAILED

☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1460, Alexandria, VA 22313-1460

37 C.F.R. § 1.2(c)

37 C.F.R. § 1.10 *

☒ with sufficient postage as first class mail.☐ as "Express Mail Post Office to Addressee"

Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____Date: 7/18/05

Signature

Tammy Knight

(Type or print name of person certifying)

* Only the date of filing § 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.0 sentence to be taken into account in determining timeliness. See § 1.705(h). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(e)) for the reply to be assessed the correct possible filing date for patent term adjustment calculation.

(Statement for Information Disclosure under 37 C.F.R. § 1.97(c) [B-1]-page 1 of 3)

NOTE: "Section 1.97(e) makes it clear that a certification could contain either of two statements. One statement is that each item of information in an information disclosure statement was cited in a search report from a patent office outside the U.S. not more than three months prior to the filing date of the statement. Under this certification, it would not matter whether any individual with a duty actually knew about any of the information cited before receiving the search report. In the alternative, the certification could state that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to the knowledge of the person signing the certification after making reasonable inquiry, was known to any individual having a duty to disclose more than three months prior to the filing of the statement." Notice of January 9, 1992, 1135 O.G. 13-25, at 13. (emphasis added). Thus: "If an item of information is submitted within three months of being cited in a communication from a foreign patent office in a counterpart foreign application, the certification can be properly made regardless of any individual's previous knowledge of the information." *Id.*, 1135 O.G. at 19. See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "The date on the communication by the foreign patent office begins the 3-month period in the same manner as the mailing of an Office action starts a 3-month shortened statutory period for reply. If the communication contains two dates, the mailing date of the communication is the one which begins the 3-month period. The date which begins the 3-month period is not the date the communication was received by a foreign associate or the date it was received by a U.S. registered practitioner. Likewise, the statement will be considered to have been filed on the date the statement was received in the Office, or on an earlier date of mailing or transmission if accompanied by a properly executed certificate of mailing or facsimile transmission under 37 CFR 1.8, or if it is in compliance with the provisions for "Express Mail" delivery under 37 C.F.R. 1.10." See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "The certification can be based on present, good faith knowledge about when information became known without a search of files being made." Thus, for example, the certification of § 1.97(e) does not preclude the use of the certification in an application by corporations whose practitioners have over the years reviewed thousands of patents and technical publications, even though they are unaware of the relevance of any one thereof to the application. Notice of January 9, 1992, 1135 O.G. 13-15, at 19.

See § 609B(5), M.P.E.P., 8th Edition:

"If an information disclosure statement includes a copy of a dated communication from a foreign patent office which clearly shows that the statement is being submitted within 3 months of the date on the communication, the copy will be accepted as the required communication. It will be assumed, in the absence of evidence to the contrary, that the communication was for a counterpart foreign application.

"In the alternative, a statement can be made if no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to the knowledge of the person signing the statement after making reasonable inquiry, neither was it known to any individual having a duty to disclose more than 3 months prior to the filing of the statement."

NOTE: A copy of the foreign search report need not be submitted with the certification. Notice of April 20, 1992 (1138 O.G. 37-41, 40).

NOTE: "The phrase 'after making reasonable inquiry' makes it clear that the individual making the statement has a duty to make reasonable inquiry regarding the facts that are being certified. The statement can be made by a registered practitioner who represents a foreign client and who relies on statements made by the foreign client as to the date the information first became known. A registered practitioner who receives information from a client without being informed whether the information was known for more than three months, however, cannot make the statement without making reasonable inquiry. For example, if an inventor gave a publication to the attorney prosecuting an application with the intent that it be cited to the Office, the attorney should inquire as to when that inventor became aware of the publication and should not submit a statement under 37 C.F.R. 1.97(e)(2) to the Office until a satisfactory response is received. The statement can be based on present, good faith knowledge about when information became known without a search of files being made." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "Although it is recognized that an individual actually becomes aware of the information in the communication from a foreign patent office sometime after it was mailed, the mailing date of such a communication, if it occurs prior to a first awareness of the same information, would determine the date for filing of an information disclosure statement without a fee" in a certification procedure under § 1.97(e). Notice of January 9, 1992, 1135 O.G. 13-25, at 19 (emphasis added).

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [B-8]—page 2 of 5)

NOTE: The mere disclosure of an item of information from a foreign patent office communication is not intended to represent an opportunity to study the substance of a item known more than three months prior to the filing of an information disclosure statement to an individual having the duty of disclosure under § 1.63. See Fed. Reg. 53,191, 53,199 (Oct. 10, 1977).

NOTE: The IDS is considered filed as of the date it is received in the PTO, or on an earlier date of mailing or transmittal if there is a properly constituted certificate of mailing or transmittal communication under 37 C.F.R. § 1.6, or if it is to be considered with the provisions for "Express Mail" delivery under 37 C.F.R. § 1.10. See § 602.3(a), M.P.E.P., 6th Edition.

NOTE: The certificate under § 1.97(c) should be made by a person who has knowledge of the facts being certified. The certificate can be made by a practitioner who represents a foreign client and who relies on documents made by the foreign client as to the date the information first became known. A practitioner who receives information from a client without being informed whether the information was known for more than three months, however, cannot make the certification without making reasonable inquiry." Notice of January 1, 1982, 1153 O.G. 19-23 at 10.

NOTE: The term counterpart foreign patent application means that a claim for priority has been made in either the U.S. application or a foreign application based on the same, or that the disclosure of the U.S. and foreign patent applications are substantially identical (i.e., an application filed in the European Patent Office claiming the same U.S. priority is deemed to be a U.S. application). Notice of April 20, 1982 (1139 O.G. 37-41, 37). See § 602.3(a), M.P.E.P., 6th Edition.

NOTE: Individuals other than the attorney, agent or inventor may comply with this section by disclosing information to the attorney, agent or inventor." 37 C.F.R. § 1.63(d) and
Individuals associated with the filing or prosecution of a patent application within the meaning of this section are:

- (1) each inventor named in the application;
- (2) each attorney or agent who procures or prosecutes the application; and
- (3) any other person who is substantially involved in the preparation or prosecution of the application and who is associated with the inventor, with the attorney or with anyone to whom there is an obligation to notify the application." 37 C.F.R. § 1.63(e).

IDENTIFICATION OF INFORMATION DISCLOSURE STATEMENT FOR WHICH THIS STATEMENT IS BEING MADE

1. This statement is being made for the Information Disclosure Statement
- ☒ accompanying this statement.
- ☐ filed _____ (date)

STATEMENT

NOTE: A statement under 37 C.F.R. § 1.97(c) need not be in the form of an oath or a declaration under 37 C.F.R. § 1.63. A statement under 37 C.F.R. § 1.97(c) by a registered practitioner or any other individual that the statement was filed within the 3-month period of either the first election by a foreign patent office or first disclosure of the information will be considered as evidence of compliance with this provision in the absence of evidence to the contrary. § 602.3(a), M.P.E.P., 6th Edition.

(Statement for Information Disclosure under 37 C.F.R. § 1.97(c) [D-4]—page 3 of 3)

2. I, the person(s) signing below state:

- ☐ that each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. 37 C.F.R. § 1.97(e)(1).

NOTE: The three month period starts from the mailing date of the foreign patent office communication. Notice of January 9, 1992, 1138 O.G. 13-25 at 18. The mailing date is the "date on the communication by the foreign patent office." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

OR

- ☒ that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to my knowledge, after making reasonable inquiry, no item of information contained in this information disclosure statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the information disclosure statement. 37 C.F.R. § 1.97(e)(2).

NOTE: "The time at which information 'was known to any individual designated in 37 C.F.R. 1.56(c)' is the time when the information was discovered in association with the application even if awareness of the materiality came later." Notice of April 20, 1992 (1138 O.G. 37-41, 40). Section 609B(5), M.P.E.P., 8th Edition.

IDENTIFICATION OF PERSON(S) MAKING THIS STATEMENT

3. The person making this statement is

(check each applicable item)

- (a) ☐ the inventor(s) who signs below

SIGNATURE OF INVENTOR

(type name of inventor who is signing)

- (b) ☐ a person who is substantively involved in the preparation or prosecution of the application, and who is associated with the inventor, with the assignee, or with anyone to whom there is an obligation to assign the application (37 C.F.R. § 1.56(c)) and who signs below.

SIGNATURE OF PERSON MAKING STATEMENT

(type name of person who is signing)

Address of person who is signing

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [3-6]—page 4 of 5)

(c) ☒ the practitioner who signs below on the basis of the information:

(check each applicable item)

- ☐ supplied by the inventor(s).
- ☐ supplied by an individual designated in § 1.56(c).
- ☒ in the practitioner's file.

Reg. No.: 28,626

Tel. No. (580) 251-3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

P.O. Box 1431

P.O. Address

Duncan, OK 73536-0440

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [8-6]—page 5 of 5)



Practitioner's Docket No. 2002-IP-009210U1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Philip D. Ngyuen, et al.

Application No: 10 / 608,291

Group No.: 3672

Filed: 06/27/2003

Examiner:

For: COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK
PERMEABILITY AND FRACTURE CONDUCTIVITY IN A SUB-

Commissioner for Patents TERRANEAN WELL

P.O. Box 1460

Alexandria, VA 22313-1460

TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
BEFORE MAILING DATE OF EITHER A FINAL ACTION
OR NOTICE OF ALLOWANCE (37 C.F.R. § 1.97(c))

NOTE: 37 C.F.R. 1.97: (c) An information disclosure statement shall be considered by the Office if filed after the period specified in paragraph (a) of this section, provided that the information disclosure statement is filed before the mailing date of any of a final action under § 1.112, a notice of allowance under § 1.911, or an action that otherwise ends prosecution in the application, and it is accompanied by one of:

- (1) The statement specified in paragraph (a) of this section; or
- (2) The fee set forth in § 1.17(c).²

NOTE: If a final action or notice of allowance is mailed in an application and later withdrawn, the application will be considered as not having had a final action or notice of allowance mailed for purposes of considering an information disclosure statement.² Notice of April 20, 1992 (6130 O.G. 37-41, 52).

CONTINUATION UNDER 37 C.F.R. §§ 1.2(a) and 1.10²
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILED

☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1460, Alexandria, VA 22313-1460

37 C.F.R. § 1.44

37 C.F.R. § 1.10²

☒ with sufficient postage on first class mail

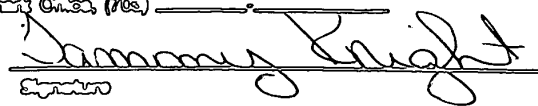
☐ as Express Mail Post Office to Addressee²

Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ hereby transmitted to the Patent and Trademark Office, (P.O.) _____

Date: 7/18/05



Tammy Knight

(Type or print name of person certifying)

² Only the date of filing of 1.0 will be the date used in a patent term adjustment calculation, through the date on any certificate of mailing or transmission under § 1.0 continues to be taken into account in determining timeliness. See § 1.705(c). Consider "Express Mail Post Office to Addressee" of 1.10 or hereby transmission of 1.6(c) for the rule to be assessed the correct possible filing date for patent term adjustment calculation.

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [Page 1 of 2])

NOTE 37 C.F.R. § 1.704(c): "A paper containing only an information disclosure statement in compliance with §§ 1.97 and 1.98 will not be considered a failure to engage in reasonable efforts to conclude prosecution (processing or examination) of the application under paragraphs (c)(6), (c)(8), (c)(9), or (c)(10) of this section if it is accompanied by a statement that each item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart application and that this communication was not received by any individual designated in § 1.56(c) more than thirty days prior to the filing of the information disclosure statement. This thirty-day period is not extendable."

NOTE "If information submitted during the period set forth in 37 C.F.R. 1.97(c) with a certification is used in a new ground of rejection on unamended claims, the next Office action will not be made final since in this situation it is clear that applicant has submitted the information to the office promptly after it has become known and the information is being submitted prior to a final determination on patentability by the Office. However, the information submitted with a certification can be used in a new ground of rejection and the next Office action made final, if the new ground of rejection was necessitated by amendment of the application by applicant. Where the information is submitted during this period with a fee, the examiner may use the information submitted, e.g., printed publication or evidence of public use, and make the next Office action final whether or not the claims have been amended, provided that no other new ground of rejection which was not necessitated by amendment to the claims is introduced by the examiner. See MPEP 708.07(h). If a new ground of rejection is introduced that is neither necessitated by an amendment to the claims nor based on the information submitted with the fee set forth in 37 C.F.R. § 1.17(p), the Office action shall not be made final." Notice of April 20, 1992 (1138 O.G. 37-41, 38).

WARNING: "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1992 (1141 O.G. 63). But see § 103(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(c) and in a request for continued examination (RCE) under § 1.114.

WARNING: No extension of time can be had under 37 C.F.R. 1.136 (a) or (b) for filing an IDS. 37 C.F.R. 1.97(f).

TIME OF TRANSMITTAL OF ACCOMPANYING INFORMATION DISCLOSURE STATEMENT

1. The information disclosure statement transmitted herewith is being filed after three months of the filing date of this national application or the date of entry of the national stage as set forth in § 1.491 in an international application or after the mailing date of the first Office action on the merits, whichever event occurred last but before the mailing date of either:

- (1) a final action under § 1.113 or
 - (2) a notice of allowance under § 1.311,
- whichever occurs first.

STATEMENT ON FEE

2. Accompanying this transmittal is

(check either A or B below)

- A. ☒ a statement as specified in 37 C.F.R. § 1.97(e).

OR

- B. ☐ the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(c). (\$180.00).

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance. [B-4]—page 2 of 3)

FEE PAYMENT

(complete this item, if applicable)

3. Applicant elects the option to pay the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(c) (\$180.00).

Fee due \$ _____

METHOD OF PAYMENT OF FEE

4.

- ☐ Attached is a ☐ check ☐ money order in the amount of \$ _____
- ☐ Authorization is hereby made to charge the amount of \$ _____
- ☒ to Deposit Account No. 08-0300
- ☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

WARNING: Credit card information should not be included on this form as it may become public.

- ☒ Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

A duplicate of this paper is attached.



SIGNATURE OF PRACTITIONER

Reg. No. 28,626

Robert A. Kent

(type or print name of practitioner)

Tel. No.: (580) 251-3125

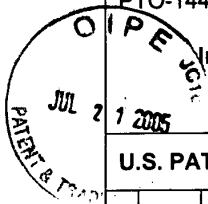
P.O. Box 1431

P.O. Address

Customer No.:

Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [B-4]—page 3 of 3)



PTO-1449		Application No. 10/608,291		Applicant(s): PHILIP D. NGUYEN, ET AL.					
Information Disclosure Citation in an Application		Docket Number		Group Art Unit	Filing Date				
		2002-IP-009210U1		3672	06/27/2003				
U.S. PATENT DOCUMENTS									
		DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE		
	1.	6,131,661	10/17/00	Conner, et al.	166	300	08/03/98		
	2.	6,143,698	11/07/00	Murphey, et al.	507	145	12/04/98		
	3.	2002/0036088 A1	03/28/02	Todd	166	300	01/09/01		
	4.	2005/0006095 A1	01/13/05	Justus, et al.	166	295	07/08/03		
FOREIGN PATENT DOCUMENTS									
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION		
							YES	NO	
NON-PATENT DOCUMENTS									
		DOCUMENT (Including Author, Title, Source, and Pertinent Pages)						DATE	
EXAMINER					DATE CONSIDERED				
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.									

IPW

Practitioner's Docket No. 2002-IP-009210U1

PATENT



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Philip D. Nguyen et al.

Application No: 10 / 608,291

Group No.: 3672

Filed: June 27, 2003

Examiner:

George Suchfield

For: Compositions And Methods For Improving
Proppant Pack Permeability And Fracture
Conductivity In A Subterranean Well

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
BEFORE MAILING DATE OF EITHER A FINAL ACTION
OR NOTICE OF ALLOWANCE (37 C.F.R. § 1.97(c))

NOTE: 37 C.F.R. 1.97: "(c) An information disclosure statement shall be considered by the Office if filed after the period specified in paragraph (a) of this section, provided that the information disclosure statement is filed before the mailing date of any of a final action under § 1.113, a notice of allowance under § 1.311, or an action that otherwise closes prosecution in the application, and it is accompanied by one of:

(1) The statement specified in paragraph (a) of this section; or

(2) The fee set forth in § 1.17(b)."

NOTE: "If a final action or notice of allowance is mailed in an application and later withdrawn, the application will be considered as not having had a final action or notice of allowance mailed for purposes of considering an information disclosure statement." Notice of April 20, 1992 (1138 O.G. 37-47, 38).

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*

(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

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37 C.F.R. § 1.8(a)

☒ with sufficient postage as first class mail.

37 C.F.R. § 1.10 *

☐ as "Express Mail Post Office to Addressee"

Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 6/4/05

Signature

Tammy Knight

(Type or print name of person certifying)

* Only the date of filing (§ 1.8) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.8(f)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [B-6]—page 1 of 3)

NOTE 37 C.F.R. § 1.704(b): "A paper containing only an information disclosure statement in compliance with §§ 1.97 and 1.98 will not be considered a failure to engage in reasonable efforts to conclude prosecution (processing or examination) of the application under paragraphs (c)(8), (c)(9), (c)(10), or (c)(11) of this section if it is accompanied by a statement that each item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart application and that this communication was not received by any individual designated in § 1.56(c) more than thirty days prior to the filing of the information disclosure statement. This thirty-day period is not extendable."

NOTE "If information submitted during the period set forth in 37 C.F.R. 1.97(c) with a certification is used in a new ground of rejection on unamended claims, the next Office action will not be made final since in this situation it is clear that applicant has submitted the information to the office promptly after it has become known and the information is being submitted prior to a final determination on patentability by the Office. However, the information submitted with a certification can be used in a new ground of rejection and the next Office action made final, if the new ground of rejection was necessitated by amendment of the application by applicant. Where the information is submitted during this period with a fee, the examiner may use the information submitted, e.g., printed publication or evidence of public use, and make the next Office action final whether or not the claims have been amended, provided that no other new ground of rejection which was not necessitated by amendment to the claims is introduced by the examiner. See MPEP 708.07(h). If a new ground of rejection is introduced that is neither necessitated by an amendment to the claims nor based on the information submitted with the fee set forth in 37 C.F.R. § 1.17(p), the Office action shall not be made final." Notice of April 20, 1988 (1138 O.G. 37-41, 38).

WARNING: "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1988 (1141 O.G. 63). But see § 109(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(c) and in a request for continued examination (RCE) under § 1.114.

WARNING: No extension of time can be had under 37 C.F.R. 1.136 (a) or (b) for filing an IDS. 37 C.F.R. 1.97(f).

TIME OF TRANSMITTAL OF ACCOMPANYING INFORMATION DISCLOSURE STATEMENT

1. The information disclosure statement transmitted herewith is being filed after three months of the filing date of this national application or the date of entry of the national stage as set forth in § 1.491 in an international application or after the mailing date of the first Office action on the merits, whichever event occurred last but before the mailing date of either:

- (1) a final action under § 1.113 or
 - (2) a notice of allowance under § 1.311,
- whichever occurs first.

STATEMENT OR FEE

2. Accompanying this transmittal is

(check either A or B below)

- A. ☒ a statement as specified in 37 C.F.R. § 1.97(e).

OR

- B. ☐ the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(d). (\$180.00).

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [B-4]—page 2 of 3)

FEE PAYMENT

(complete this item, if applicable)

3. Applicant elects the option to pay the fee set forth in 37 C.F.R. § 1.17(p) for submission of an information disclosure statement under § 1.97(c) (\$180.00).

Fee due \$ _____

METHOD OF PAYMENT OF FEE

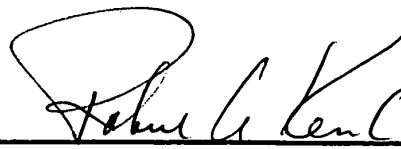
4.

- ☐ Attached is a ☐ check ☐ money order in the amount of \$ _____
- ☐ Authorization is hereby made to charge the amount of \$ _____
- ☐ to Deposit Account No. _____
- ☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

WARNING: Credit card information should not be included on this form as it may become public.

- ☐ Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

A duplicate of this paper is attached.



SIGNATURE OF PRACTITIONER

Reg. No. 28,626

Robert A. Kent

(type or print name of practitioner)

Tel. No.: (580) 251-3125

P.O. Box 1431

P.O. Address

Customer No.:

Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement before Mailing Date of Either a Final Action Or Notice of Allowance [8-4]—page 3 of 3)

Practitioner's Docket No. _____

PATENT**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: Philip D. Nguyen et al.

Group No. 3672

Application No.: 10 / 608,291

Examiner: George Suchfield

Filed: June 27, 2003

For: Compositions And Methods For Improving Proppant Pack Permeability
And Fracture Conductivity In A Subterranean Well

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**STATEMENT FOR INFORMATION DISCLOSURE UNDER
37 C.F.R. § 1.97(e)**

NOTE: A statement must state either: "(1) that each item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement, or (2) that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and to the knowledge of the person signing the statement after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the information disclosure statement." 37 C.F.R. § 1.97(e).

Under the first statement under § 1.97(e), it does not matter whether any individual with a duty of disclosure actually knew about any of the information cited before receiving the search report. The date on the communication by the foreign patent office begins the 3-month period in the same manner as the mailing of an Office action starts a 3-month shortened statutory period for reply. See § 609B(5), M.P.E.P., 8th Edition.

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10 *

☒ with sufficient postage as first class mail.

☐ as "Express Mail Post Office to Addressee"

Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 6/14/05Signature Tammy KnightTammy Knight

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.8(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [8-6]—page 1 of 5)

NOTE: "Section 1.97(e) makes it clear that a certification could contain either of two statements. One statement is that each item of information in an information disclosure statement was cited in a search report from a patent office outside the U.S. not more than three months prior to the filing date of the statement. Under this certification, it would not matter whether any individual with a duty actually knew about any of the information cited before receiving the search report. In the alternative, the certification could state that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to the knowledge of the person signing the certification after making reasonable inquiry, was known to any individual having a duty to disclose more than three months prior to the filing of the statement." Notice of January 9, 1992, 1135 O.G. 13-25, at 13. (emphasis added). Thus: "If an item of information is submitted within three months of being cited in a communication from a foreign patent office in a counterpart foreign application, the certification can be properly made regardless of any individual's previous knowledge of the information." *Id.*, 1135 O.G. at 19. See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "The date on the communication by the foreign patent office begins the 3-month period in the same manner as the mailing of an Office action starts a 3-month shortened statutory period for reply. If the communication contains two dates, the mailing date of the communication is the one which begins the 3-month period. The date which begins the 3-month period is not the date the communication was received by a foreign associate or the date it was received by a U.S. registered practitioner. Likewise, the statement will be considered to have been filed on the date the statement was received in the Office, or on an earlier date of mailing or transmission if accompanied by a properly executed certificate of mailing or facsimile transmission under 37 CFR 1.8, or if it is in compliance with the provisions for "Express Mail" delivery under 37 C.F.R. 1.10." See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "The certification can be based on present, good faith knowledge about when information became known without a search of files being made." Thus, for example, the certification of § 1.97(e) does not preclude the use of the certification in an application by corporations whose practitioners have over the years reviewed thousands of patents and technical publications, even though they are unaware of the relevance of any one thereof to the application. Notice of January 9, 1992, 1135 O.G. 13-15, at 19.

See § 609B(5), M.P.E.P., 8th Edition:

"If an information disclosure statement includes a copy of a dated communication from a foreign patent office which clearly shows that the statement is being submitted within 3 months of the date on the communication, the copy will be accepted as the required communication. It will be assumed, in the absence of evidence to the contrary, that the communication was for a counterpart foreign application.

"In the alternative, a statement can be made if no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to the knowledge of the person signing the statement after making reasonable inquiry, neither was it known to any individual having a duty to disclose more than 3 months prior to the filing of the statement."

NOTE: A copy of the foreign search report need not be submitted with the certification. Notice of April 20, 1992 (1138 O.G. 37-41, 40).

NOTE: "The phrase 'after making reasonable inquiry' makes it clear that the individual making the statement has a duty to make reasonable inquiry regarding the facts that are being certified. The statement can be made by a registered practitioner who represents a foreign client and who relies on statements made by the foreign client as to the date the information first became known. A registered practitioner who receives information from a client without being informed whether the information was known for more than three months, however, cannot make the statement without making reasonable inquiry. For example, if an inventor gave a publication to the attorney prosecuting an application with the intent that it be cited to the Office, the attorney should inquire as to when that inventor became aware of the publication and should not submit a statement under 37 C.F.R. 1.97(e)(2) to the Office until a satisfactory response is received. The statement can be based on present, good faith knowledge about when information became known without a search of files being made." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "Although it is recognized that an individual actually becomes aware of the information in the communication from a foreign patent office sometime after it was mailed, the mailing date of such a communication, if it occurs prior to a first awareness of the same information, would determine the date for filing of an information disclosure statement without a fee" in a certification procedure under § 1.97(e). Notice of January 9, 1992, 1135 O.G. 13-25, at 19 (emphasis added).

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [8-5]—page 2 of 5)

NOTE: The mere absence of an item of information from a foreign patent office communication is not intended to represent an opportunity to delay the submission of a item known more than three months prior to the filing of an information disclosure statement to an individual having the duty of disclosure under § 1.56. 62 Fed. Reg. 53,131, 53,150 (Oct. 10, 1997).

NOTE: The IDS is considered filed as of the date it is received in the PTO, or on an earlier date of mailing or transmission if done so with a properly executed certificate of mailing or facsimile transmission under 37 C.F.R. § 1.8, or if it is in compliance with the provisions for "Express Mail" delivery under 37 C.F.R. § 1.10. See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "The certification under § 1.97(e) should be made by a person who has knowledge of the facts being certified. The certification can be made by a practitioner who represents a foreign client and who relies on statements made by the foreign client as to the date the information first became known. A practitioner who receives information from a client without being informed whether the information was known for more than three months, however, cannot make the certification without making reasonable inquiry." Notice of January 9, 1992, 1135 O.G. 13-25 at 19.

NOTE: "The term counterpart foreign patent application means that a claim for priority has been made in either the U.S. application or a foreign application based on the other, or that the disclosures of the U.S. and foreign patent applications are substantively identical (e.g., an application filed in the European Patent Office claiming the same U.K. priority as claimed in the U.S. application)." Notice of April 20, 1992 (1138 O.G. 37-41, 39). See § 609B(5), M.P.E.P., 8th Edition.

NOTE: "Individuals other than the attorney, agent or inventor may comply with this section by disclosing information to the attorney, agent or inventor." 37 C.F.R. § 1.56(d) and

"Individuals associated with the filing or prosecution of a patent application within the meaning of this section are:

- (1) each inventor named in the application;
- (2) each attorney or agent who prepares or prosecutes the application; and
- (3) every other person who is substantively involved in the preparation or prosecution of the application and who is associated with the inventor, with the assignee or with anyone to whom there is an obligation to assign the application." 37 C.F.R. § 1.56(c).

IDENTIFICATION OF INFORMATION DISCLOSURE STATEMENT FOR WHICH THIS STATEMENT IS BEING MADE

1. This statement is being made for the Information Disclosure Statement

- ☒ accompanying this statement.
☐ filed _____ (date)

STATEMENT

NOTE: A statement under 37 C.F.R. § 1.97(e) need not be in the form of an oath or a declaration under 37 C.F.R. § 1.68. A statement under 37 C.F.R. § 1.97(e) by a registered practitioner or any other individual that the statement was filed within the 3-month period of either the first citation by a foreign patent office or first discovery of the information will be accepted as dispositive of compliance with this provision in the absence of evidence to the contrary. § 609B(5), M.P.E.P., 8th Edition.

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [8-8]—page 3 of 5)

2. I, the person(s) signing below state:

- ☒ that each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. 37 C.F.R. § 1.97(e)(1).

NOTE: The three month period starts from the mailing date of the foreign patent office communication. Notice of January 9, 1992, 1135 O.G. 13-25 at 19. The mailing date is the "date on the communication by the foreign patent office." Notice of April 20, 1992 (1138 O.G. 37-41, 38).

OR

- ☐ that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application and, to my knowledge, after making reasonable inquiry, no item of information contained in this information disclosure statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the information disclosure statement. 37 C.F.R. § 1.97(e)(2).

NOTE: "The time at which information 'was known to any individual designated in 37 C.F.R. 1.56(c)' is the time when the information was discovered in association with the application even if awareness of the materiality came later." Notice of April 20, 1992 (1138 O.G. 37-41, 40). Section 6098(5), M.P.E.P., 8th Edition.

IDENTIFICATION OF PERSON(S) MAKING THIS STATEMENT

3. The person making this statement is

(check each applicable item)

- (a) ☐ the inventor(s) who signs below

SIGNATURE OF INVENTOR

(type name of inventor who is signing)

- (b) ☐ a person who is substantively involved in the preparation or prosecution of the application, and who is associated with the inventor, with the assignee, or with anyone to whom there is an obligation to assign the application (37 C.F.R. § 1.56(c)) and who signs below.

SIGNATURE OF PERSON MAKING STATEMENT

(type name of person who is signing)

Address of person who is signing

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [8-8]—page 4 of 5)

(c) ☒ the practitioner who signs below on the basis of the information:

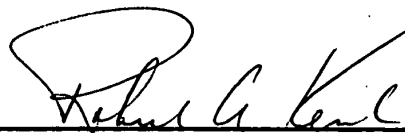
(check each applicable item)

- ☐ supplied by the inventor(s).
- ☐ supplied by an individual designated in § 1.56(c).
- ☒ in the practitioner's file.

Reg. No.: 28,626

Tel. No. (251) 3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

P.O. Box 1431

P.O. Address

Duncan, OK 73536-0440

(Statement for Information Disclosure under 37 C.F.R. § 1.97(e) [8-8]—page 5 of 5)



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Philip D. Nguyen et al.)	
)	Art Unit: 3672
Serial No.:	10/608,291)	
)	
Filed:	June 27, 2003)	Examiner: George Suchfield
)	
For:	Compositions And Methods For Improving)	
	Proppant Pack Permeability And Fracture)	
	Conductivity In A Subterranean Well)	

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

COMMISSIONER FOR PATENTS
Alexandria, VA 22313-1450

SIR:

The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

U. S. PATENTS

U.S. Patent Number 3,173,484 issued 03/16/1965 to Jimmie L. Huitt, et al;

U.S. Patent Number 3,195,635 issued 07/20/1965 to Clarence R. Fast;

U.S. Patent Number 3,302,719 issued 02/07/1967 to Paul W. Fischer;

U.S. Patent Number 3,364,995 issued 01/23/1968 to Bobby L. Atkins, et al;

U.S. Patent Number 3,366,178 issued 01/30/1968 to William T. Malone, et al;

U.S. Patent Number 3,455,390 issued 07/15/1969 to J. P. Gallus;

U.S. Patent Number 3,968,840 issued 07/13/1976 to Jack F. Tate;

U.S. Patent Number 3,998,744 issued 12/21/1976 to Vernon W. Arnold, et al; and

U.S. Patent Number 4,068,718 issued 01/17/1978 to Claude E. Cooke, Jr., et al.

FOREIGN PATENTS

The foreign art contained in this supplemental information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three (3) months prior to the filing of the information disclosure statement.

International Publication Number WO 2004/007905 A1 published 01/22/2004 to Ralph Edmund Harris, et al;

International Publication Number WO 00/57022 published 09/28/2000 to Ralph Edmund Harris, et al;

International Publication Number WO 01/02698 A1 published 01/11/2001 to Ralph Edmund Harris, et al.

OTHER MATERIALS

Y. Chiang, et al.: "Hydrolysis of Ortho Esters: Further Investigation of the Factors Which Control the Rate-Determining Step," **Engineering Information Inc., New York, NY**, Vol. 105, No. 23, (XP-002322842), November 16, 1983;

M. Ahmad, et al.: "Ortho Ester Hydrolysis: Direct Evidence for a Three-Stage Reaction Mechanism," **Engineering Information Inc., New York, NY**, Vol. 101, No. 10, (XP-002322843), May 9, 1979; and

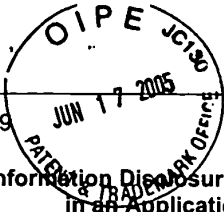
Foreign communication from a related counterpart (International Application PCT/GB2004/005309, filed 12/17/2004), mailing dated 04/13/2005.

Copies of the aforementioned non-patent references and Form PTO-1449 are submitted
herewith.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Robert A. Kent". The signature is fluid and cursive, with the first name "Robert" and last name "Kent" being clearly legible.

Robert A. Kent
Registration No. 28,626
Halliburton Energy Services
P. O. Box 1431
Duncan, OK 73536-0440
580-251-3125



PTO-1449 Information Disclosure Citation in an Application		Application No. 10/608,291		Applicant(s): PHILIP NGUYEN ET AL.	
Docket Number 2002-IP-009210U1		Group Art Unit 3672		Filing Date June 27, 2003	

U.S. PATENT DOCUMENTS						
	DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE
1.	3,173,484	03/16/65	Huitt, et al.	166	280.1	09/02/58
2.	3,195,635	07/20/65	Fast	166	280.1	05/23/63
3.	3,302,719	02/07/67	Fischer	166	280.2	01/25/65
4.	3,364,995	01/23/68	Atkins, et al.	166	280.1	02/14/66
5.	3,366,178	01/30/68	Malone, et al.	166	280.1	09/10/65
6.	3,455,390	07/15/69	Gallus	166	295	12/03/65
7.	3,968,840	07/13/76	Tate	166	280.1	05/25/73
8.	3,998,744	12/21/76	Arnold, et al.	507	269	04/16/75
9.	4,068,718	01/17/78	Cooke, Jr., et al.	166	280.2	10/26/76

FOREIGN PATENT DOCUMENTS							
	DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
						YES	NO
1.	WO 2004/007905	01/22/04	PCT	E21B	43/27	X	
2.	WO 2000/57022	09/28/00	PCT	E21B	37/06	X	
3.	WO 2001/02698	01/11/01	PCT	E21B	43/27	X	

NON-PATENT DOCUMENTS		
	DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE
1.	Y. CHIANG ET AL.: "HYDROLYSIS OF ORTHO ESTERS: FURTHER INVESTIGATION OF THE FACTORS WHICH CONTROL THE RATE-DETERMINING STEP," ENGINEERING INFORMATION INC., NY, NY, VOL. 105, No. 23 (XP-002322842)	11/16/83
2.	M. AHMAD, ET AL.: "ORTHO ESTER HYDROLYSIS: DIRECT EVIDENCE FOR A THREE-STAGE REACTION MECHANISM," ENGINEERING INFORMATION INC., NY, NY, VOL. 101, No. 10 (XP-002322843)	05/09/79

EXAMINER	DATE CONSIDERED
----------	-----------------

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/608,291	06/27/2003	Philip D. Nguyen	2002-IP-009210U1	8521
7590	05/17/2005			
Robert A. Kent Halliburton Energy Services 2600 South 2nd Street Duncan, OK 73536				
EXAMINER SUCHFIELD, GEORGE A				
ART UNIT		PAPER NUMBER		
3672				

DATE MAILED: 05/17/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No.	Applicant(s)	
	10/608,291	NGUYEN ET AL.	
	Examiner	Art Unit	
	George Suchfield	3672	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1) ☒ Responsive to communication(s) filed on 21 March 2005.

2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.

3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4) ☒ Claim(s) 1-72 is/are pending in the application.

4a) Of the above claim(s) 39-72 is/are withdrawn from consideration.

5) ☐ Claim(s) _____ is/are allowed.

6) ☒ Claim(s) 1-5, 7-9, 12-15, 17-27 and 30-33 is/are rejected.

7) ☒ Claim(s) 6, 10, 11, 16, 28, 29 and 34 is/are objected to.

8) ☒ Claim(s) 1-72 are subject to restriction and/or election requirement.

Application Papers

9) ☐ The specification is objected to by the Examiner.

10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a) ☐ All b) ☐ Some * c) ☐ None of:

1. ☐ Certified copies of the priority documents have been received.

2. ☐ Certified copies of the priority documents have been received in Application No. _____.

3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date 3/21/05; 1/25/05

4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____

5) ☐ Notice of Informal Patent Application (PTO-152)

6) ☐ Other: _____

1. Restriction to one of the following inventions is required under 35 U.S.C. 121:
 - I. Claims 1-38, drawn to method of fracturing and propping a subterranean formation, classified in class 166, subclass 280.2.
 - II. Claims 39-72, drawn to a composition, classified in class 507, subclass 219.

The inventions are distinct, each from the other because of the following reasons:

2. Inventions I and II are related as product and process of use. The inventions can be shown to be distinct if either or both of the following can be shown: (1) the process for using the product as claimed can be practiced with another materially different product or (2) the product as claimed can be used in a materially different process of using that product (MPEP § 806.05(h)). In the instant case the composition could be used in other applications or processes, such as in gravel packing a well or in the treatment of other permeable material, such as in a soil remediation or soil stabilization process. Also, the composition would appear to have utility as a filter media in an above-ground water treatment or separation process.
3. Because these inventions are distinct for the reasons given above and have acquired a separate status in the art as shown by their different classification, restriction for examination purposes as indicated is proper.
4. Because these inventions are distinct for the reasons given above and have acquired a separate status in the art because of their recognized divergent subject matter, restriction for examination purposes as indicated is proper.
5. During a telephone conversation with Robert A. Kent on May 4, 2005 a provisional election was made without traverse to prosecute the invention of Group I, claims 1-38. Affirmation of this election must be made by applicant in replying to this Office action. Claims

39-72 stand withdrawn from further consideration by the examiner, 37 CFR 1.142(b), as being drawn to a non-elected invention.

6. Applicant is reminded that upon the cancellation of claims to a non-elected invention, the inventorship must be amended in compliance with 37 CFR 1.48(b) if one or more of the currently named inventors is no longer an inventor of at least one claim remaining in the application. Any amendment of inventorship must be accompanied by a request under 37 CFR 1.48(b) and by the fee required under 37 CFR 1.17(i).

7. The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

8. Claims 14 and 32 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Claims 14 and 32 are deemed indefinite with respect to the recitation of “a desirable number of voids”. Since the term “desirable” is subjective or non-specific, these claims fails to “distinctly claim the invention”, as required by the statute.

9. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(a) the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicant for a patent.

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

(e) the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an

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international application filed under the treaty defined in section 351(a) shall have the effects for purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.

10. Claims 1, 2, 7-9, 12, 14, 16, 17-21, 25-27, 30, 32, 34 and 35 are rejected under 35

U.S.C. 102(a) as being anticipated by Cooke, Jr. (2003/0060374).

In one embodiment, Cooke, Jr. (note Figure 2c) may employ a proppant composition in the fracturing process comprising a mixture or composite of proppant particles and a degradable polymer, as called for in independent claims 1 and 20.

Cooke, Jr. further discloses one or more of the degradable polymers set forth in claims 8, 12, 18, 26 and 30 and may further use a plasticizer, as called for in claims 9 and 27.

As per claim 14 and 32 it appears from the illustration in Figure 2c that a “desirable” number of voids will be present up degradation and removal of the degradable polymer phase.

As per claims 16 and 34, note that the proppant composition of Figure 2c of Cooke, Jr., and thus the degradable polymer component, appear to have a “rod-like” shape, as recited.

As per claim 35, it is deemed that the resulting void space(s) created by the degradation of the degradable polymer will necessarily be “channel-like” in shape, e.g., due to the accompanying or resulting fluid-flow through the proppant matrix.

11. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

12. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various

claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

13. Claim 3, 15, 33 and 36-38 are rejected under 35 U.S.C. 103(a) as being unpatentable over Cooke, Jr. (2003/0060374).

The size range of the proppant particles utilized in the method of Cooke, Jr., as recited in claim 3, and the resulting proppant matrix conductivity recited in claims 36-38 would have been an obvious matter of choice or design in carrying out the fracturing process of Cooke, Jr. based on, e.g., the characteristics or composition of the subterranean formation(s) actually encountered in the field and/or based on routine experimentation for process optimization or economic feasibility.

Similarly, the precise amount of degradable polymer present in the proppant composition utilized by Cooke, Jr., as called for in claims 15 and 33, would also have been an obvious matter of choice or design in carrying out the fracturing process of Cooke, Jr. based on, e.g., the characteristics or composition of the subterranean formation(s) actually encountered in the field, such as the structural integrity and/or degree of consolidation of the formation matrix.

14. Claims 1-5, 7, 8, 14, 15, 17, 19, 20, 22, 23, 25, 26, 32, 33 and 35 are rejected under 35 U.S.C. 102(b) as being anticipated by Betzold (6,328,105).

Betzold (note col. 2, lines 33-62; col. 3, line 42 - col. 4, line 15) discloses a process of fracturing and propping a subterranean formation(s) with a proppant composition or composite,

especially in view of the coating on the proppant particles, comprising a mixture of a coated, bondable propping particles and removable particles, wherein such removable particles may decompose or degrade within the formation fracture, as called for in independent claims 1 and 20.

As per claim 3, the average particle size range set forth in the EXAMPLE of 800-1000 microns would appear to fall within the mesh particle size range recited.

As per claims 4, 5, 22, 23, the conventional coated particles or coating formulations referred to in Betzold (note col. 3, lines 17-41) would appear to encompass those recited.

Betzold further discloses one or more of the degradable polymers set forth in claims 8, 26.

As per claim 14 and 32 it is deemed that in the operation of the Betzold fracturing process, a “desirable” number of voids will be inherently or necessarily present upon degradation and removal of the degradable polymer phase, in order to allow flowback and production of mineral fluids.

As per claims 15 and 33, the exemplary range set forth in Betzold (note col. 5, lines 7-17) of 10-30 % falls within the recited range of “0.1% to about 30%”.

As per claim 35, it is deemed that the resulting void space(s) created by the degradation of the degradable polymer in the process of Betzold will necessarily be “channel-like” in shape, e.g., due to the accompanying or resulting fluid-flow through the proppant matrix.

15. Claims 36-38 are rejected under 35 U.S.C. 103(a) as being unpatentable over Betzold (6,328,105).

To provide resulting proppant matrix conductivity recited in claims 36-38 would have been an obvious matter of choice or design in carrying out the fracturing process of Betzold based

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on, e.g., the characteristics or composition of the subterranean formation(s) actually encountered in the field and/or based on routine experimentation for process optimization or economic feasibility.

16. Claim 9, 12, 27 and 30 are rejected under 35 U.S.C. 103(a) as being unpatentable over Betzold (6,328,105) as applied to claim 1 above, and further in view of Cooke, Jr. (2003/0060374).

As per claims 9 and 27, it would have been obvious to one of ordinary skill in the art to which the invention pertains, to employ a degradable polymer which further comprises a plasticizer and/or which has been plasticized in the proppant composition utilized in the fracturing and propping process of Betzold, as taught by Cooke, Jr. (note Para [0027]), applied above, in order to impart improved characteristics to such degradable polymer, such as decreased viscosity.

As per claims 12 and 30, it would have been further obvious to one of ordinary skill in the art to which the invention pertains, to employ a poly(lactide) as the degradable polymer in the proppant composition utilized in the fracturing and propping process of Betzold, as taught by Cooke, Jr. (note Para [0023]), applied above, based upon, e.g., the availability and/or cost effectiveness of poly(lactide) relative to other conventional degradable polymers.

17. Claim 13 and 31 are rejected under 35 U.S.C. 103(a) as being unpatentable over Betzold (6,328,105) as applied to claim 1 above, and further in view of Cooke, Jr. (2003/0060374) and Cooke, Jr. et al (4,068,718).

As per claims 13 and 31, it would have been obvious to one of ordinary skill in the art to which the invention pertains, to employ a poly(lactide) as the degradable polymer in the proppant

composition utilized in the fracturing and propping process of Betzold, as taught by Cooke, Jr. (note Para [0023]), applied above, based upon, e.g., the availability and/or cost effectiveness of poly(lactide) relative to other conventional-degradable polymers. It would also have been obvious to employ bauxite as the proppant particles in the process of Betzold, as taught by Cooke, Jr. et al (note col. 2, lines 13-34), in order to impart enhanced compressive strength and resistance to formation fluids.

18. Claims 1, 3, 7, 14, 17, 19, 20, 21, 25, 32 and 35 are rejected under 35 U.S.C. 102(b) as being anticipated by Atkins et al (3,364,995).

Atkins et al (note col. 4, line 64 – col. 5, line 2) discloses a process of fracturing and propping a subterranean formation(s) employing a proppant composition in the fracturing fluid which comprises a mixture or composite of a proppant particulate and a degradable material, such as a solid spacer material which chemically decomposes in the fracture(s), as called for in independent claims 1 and 20.

As per claim 3, the recited range of 10-60 mesh falls within or is encompassed by the proppant size range in Atkins et al (note col. 2, lines 33-57) of 4-80 mesh.

As per claims 7 and 25, Atkins et al may employ either a degradable polymer, i.e., a polysulfone and a dehydrated salt, such as a carbonate as the degradable component in the proppant mixture.

As per claims 14 and 32, it is deemed that in the operation of the Atkins et al fracturing process, a “desirable” number of voids will be inherently or necessarily present upon degradation and removal of the degradable polymer phase, in order to allow flowback and production of mineral fluids.

As per claim 35, it is deemed that the resulting void space(s) created by the degradation of the degradable polymer, carbide or carbonate component in the process of Atkins will necessarily be "channel-like" in shape, e.g., due to the accompanying or resulting fluid-flow through the proppant matrix.

19. Claims 36-38 are rejected under 35 U.S.C. 103(a) as being unpatentable over Atkins et al (3,364,995).

To provide resulting proppant matrix conductivity recited in claims 36-38 would have been an obvious matter of choice or design in carrying out the fracturing process of Atkins et al based on, e.g., the characteristics or composition of the subterranean formation(s) actually encountered in the field and/or based on routine experimentation for process optimization or economic feasibility.

20. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure.

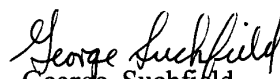
It is noted that the reference to Huitt (3,173,484) also discloses a method of fracturing and propping a subterranean formation utilizing a proppant mixture or composite of proppant particles and a soluble or decomposable component. Hence, it is deemed cumulative to the references applied above against one or more of the pending claims, such as claims 1 and 20. Accordingly, any amendment(s) to the pending claims in response to this Office action must distinguish over Huitt'484, as well.

21. Claims 6, 10, 11, 16, 24, 28, 29 and 34 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to George Suchfield whose telephone number is 571-272-7036. The examiner can normally be reached on M-F (6:30 - 3:00).

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, David Bagnell can be reached on 571-272-6999. The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).


George Suchfield
Primary Examiner
Art Unit 3672

Gs
May 6, 2005

Notice of References Cited	Application/Control No. 10/608,291	Applicant(s)/Patent Under Reexamination NGUYEN ET AL.	
	Examiner George Suchfield	Art Unit 3672	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
	A	US-3,173,484	03-1965	HUITT JIMMIE L; et. al.	166/280.1
	B	US-3,195,635	07-1965	FAST CLARENCE R	166/280.1
	C	US-3,302,719	02-1967	FISCHER PAUL W	166/280.2
	D	US-3,364,995	01-1968	ATKINS BOBBY L; et. al.	166/280.1
	E	US-3,366,178	01-1968	MALONE WILLIAM T; et. al.	166/280.1
	F	US-3,455,390	07-1969	GALLUS JULIUS P	166/295
	G	US-3,968,840	07-1976	Tate, Jack F.	166/280.1
	H	US-3,998,744	12-1976	Arnold et al.	507/269
	I	US-4,068,718	01-1978	Cooke et al.	166/280.2
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

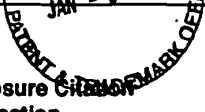
NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
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	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.



PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al				
Information Disclosure Citation in an Application		Docket Number 2002-IP-009210U1		Group Art Unit 3672	Filing Date 06/27/2003			
U.S. PATENT DOCUMENTS								
		6,763,888 B1	07/20/04	Harris, et al	166	305.1	03/20/00	
GS		US 2004/0261993A1 (US Pat. App. Ser. No. 10/608,319)	12/30/04	Nguyen (Ref. No. 2003-IP-010077U1)	166	276	06/27/03	
	1	US 2004/0261995A1 (US Pat. App. Ser. No. 10/608,291)	12/30/04	Nguyen, et al (Ref. No. 2002-IP-009210U1)	166	279	06/27/03	
	1	US 2004/0261996A1 (US Pat. App. Ser. No. 10/609,031)	12/30/04	Munoz, Jr., et al (Ref. No. 2002-IP-009052U1)	166	279	06/27/03	
GS		US 2004/0261999A1 (US Pat. App. Ser. No. 10/608,373)	12/30/04	Nguyen (Ref. No. 2003-IP-010077U2)	166	292	06/27/03	
FOREIGN PATENT DOCUMENTS								
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
							Yes	No
GS		EP 0 879 935 A3	10-02-99	Europe	E21B	43/26	X	
EXAMINER George Suchfield					DATE CONSIDERED 5/4/05			
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PTO-1449 Information Disclosure Statement in an Application		Application No. 10/608,291	Applicant(s): PHILIP D. NGUYEN, ET AL	
Docket Number 2002-IP-009210U1		Group Art Unit 3672	Filing Date 06/27/2003	

U.S. PATENT DOCUMENTS							
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<input checked="" type="checkbox"/>	1.	4,817,721	04/04/89	Pober	166	295	12/14/87
<input type="checkbox"/>	2.	5,142,023	08/25/92	Gruber, et al	528	354	01/24/92
<input type="checkbox"/>	3.	5,247,059	09/21/93	Gruber, et al	528	354	08/24/92
<input type="checkbox"/>	4.	5,359,026	10/25/94	Gruber	528	354	07/30/93
<input type="checkbox"/>	5.	5,475,080	12/12/95	Gruber, et al	528	354	03/22/93
<input type="checkbox"/>	6.	5,484,881	01/16/96	Gruber, et al	528	354	08/23/93
<input type="checkbox"/>	7.	5,536,807	07/16/96	Gruber, et al	528	354	08/23/93
<input type="checkbox"/>	8.	5,594,095	01/14/97	Gruber, et al	528	354	07/27/94
<input type="checkbox"/>	9.	5,839,510	11/24/98	Weaver, et al	166	276	01/14/97
<input type="checkbox"/>	10.	5,849,401	12/15/98	El-Afandi, et al	428	215	05/03/96
<input type="checkbox"/>	11.	6,326,458 B1	12/04/01	Gruber, et al	528	354	10/07/93
<input type="checkbox"/>	12.	6,439,309 B1	08/27/02	Matherly, et al	166	276	12/13/00
<input checked="" type="checkbox"/>	13.	6,488,091 B1	12/03/02	Weaver, et al	166	300	06/11/01

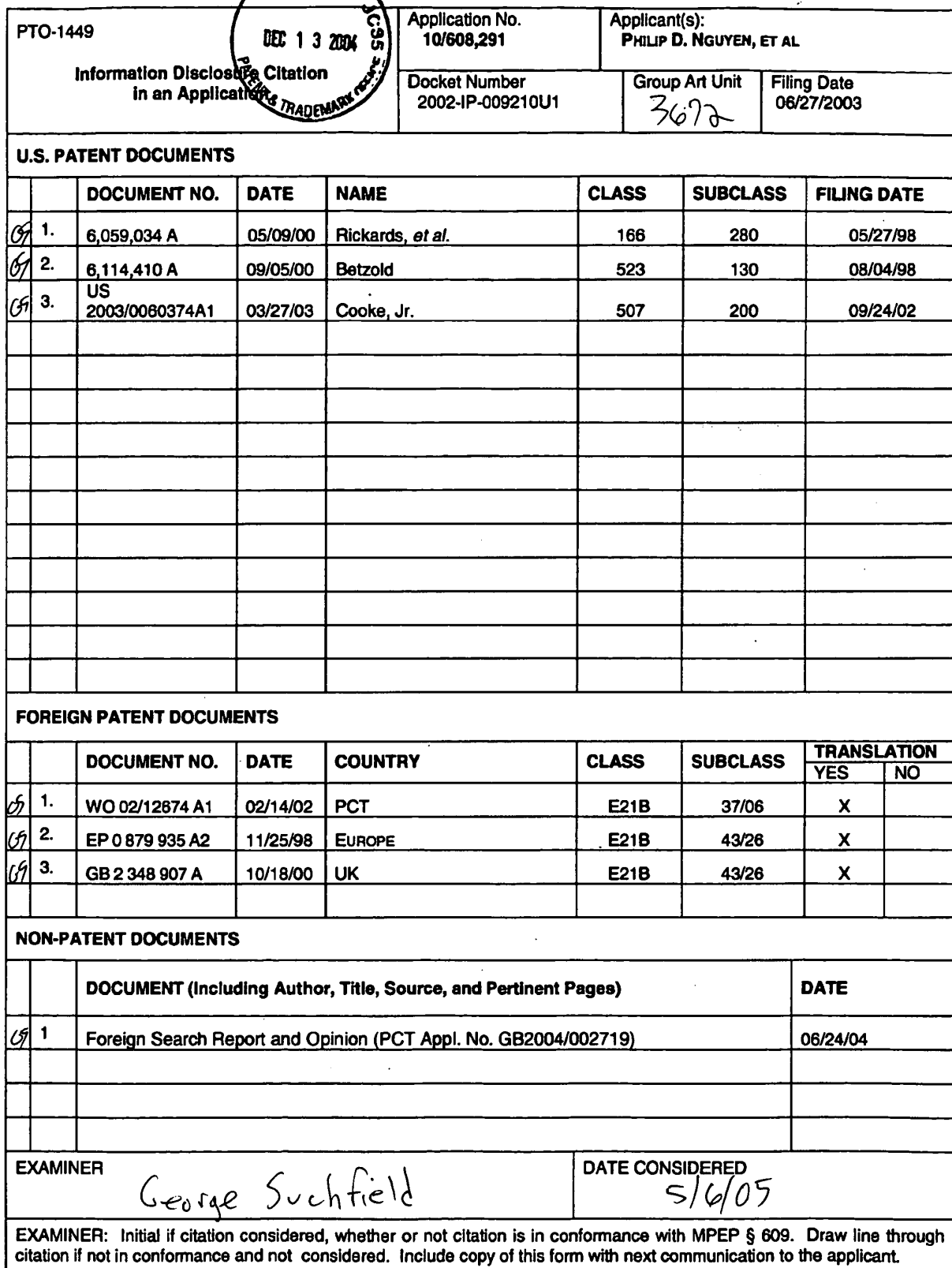
FOREIGN PATENT DOCUMENTS							
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<input type="checkbox"/>	B.	WO 94/07949 A1	04/14/94	PCT	C08K	11/00	X
<input type="checkbox"/>	C.	WO 94/08078 A1	04/14/94	PCT	D01F	6/62	X
<input checked="" type="checkbox"/>	D.	WO 94/08090 A1	04/14/94	PCT	D21H	19/28	X

NON-PATENT DOCUMENTS	
DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE

EXAMINER <div style="font-size: 1.2em; font-family: cursive;">George Suchfield</div>	DATE CONSIDERED <div style="font-size: 1.2em; font-family: cursive;">5/6/05</div>
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PTO-1449 Information Disclosure Citation in an Application		Application No. 10/608,291 Docket Number 2002-IP-009210U1		Applicant(s) Philip D. Nguyen, et al Group Art Unit 3672 Filing Date 06/27/2003		
U.S. PATENT DOCUMENTS						
	DOCUMENT NO.	ISSUE/ PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
C	2,703,316	03-01-55	Palmer	260	78.3	06-05-51
C	3,272,650	09-13-66	MacVittie	134	7	02-21-63
	3,819,525	06-25-74	Hattenbrun	252	132	08-21-72
	3,912,692	10-14-75	Casey <i>et al.</i>	260	78.3	09-24-74
	4,172,066	10-23-79	Zweigle <i>et al.</i>	260	29.6TA	09-26-77
	4,460,052	07-17-84	Gockel	175	72	08-10-81
	4,498,995	02-12-85	Gockel	252	8.5LC	07-01-83
	4,797,262	01-10-89	Dewitz	422	142	06-03-87
	5,249,628	10-05-93	Surjaatmadja	166	305	09-29-92
	5,295,542	03-22-94	Cole, <i>et al.</i>	166	278	10-05-92
	5,325,923	07-05-94	Surjaatmadja, <i>et al.</i>	166	308	09-30-93
	5,330,005	07-19-94	Card, <i>et al.</i>	166	280	04-05-93
	5,360,068	11-01-94	Sprunt, <i>et al.</i>	166	259	04-19-93
	5,363,916	11-15-94	Himes, <i>et al.</i>	166	276	06-16-93
	5,373,901	12-20-94	Norman, <i>et al.</i>	166	300	07-27-93
	5,386,874	02-07-95	Laramay, <i>et al.</i>	166	300	11-08-93
	5,396,957	03-14-94	Surjaatmadja, <i>et al.</i>	166	308	03-04-94
	5,402,846	04-04-95	Jennings, Jr., <i>et al.</i>	166	259	11-15-93
	5,464,060	11-07-95	Hale, <i>et al.</i>	166	293	04-12-94
	5,497,830	03-12-96	Boles, <i>et al.</i>	166	300	04-06-95
	5,499,678	03-19-96	Surjaatmadja, <i>et al.</i>	166	298	08-02-94
	5,505,787	04-09-96	Yamaguchi	134	4	01-28-94
	5,512,071	04-30-96	Yam, <i>et al.</i>	51	307	02-25-94
	5,604,186	02-18-97	Hunt, <i>et al.</i>	507	204	02-15-95
C	5,670,473	09-23-97	Scepanski	510	445	06-06-95
EXAMINER George Suchfield				DATE CONSIDERED 5/6/05		
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PTO-1449 Information Disclosure Citation in an Application		Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al	
		Docket Number 2002-IP-009210U1		Group Art Unit 3672	Filing Date 06/27/2003

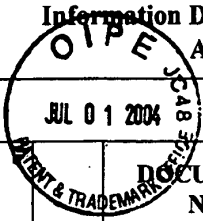
U.S. PATENT DOCUMENTS							
		DOCUMENT NO.	ISSUE/ PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
CG		5,698,322	12-16-97	Tsai, et al.	428	373	12-02-96
		5,765,642	06-16-98	Surjaatmadja	166	297	12-23-96
		5,833,000	11-10-98	Weaver, et al.	166	276	02-18-97
		5,853,048	12-29-98	Weaver, et al.	166	279	04-21-98
		5,893,416	04-13-99	Read	166	304	11-28-97
		5,964,291	10-12-99	Bourne, et al.	166	279	02-28-96
		6,004,400	12-21-99	Bishop, et al.	134	2	07-09-97
		6,024,170	02-15-00	McCabe, et al.	166	300	06-03-98
		6,028,113	02-22-00	Scepanski	514	643	09-27-95
		6,123,965	09-26-00	Jacob, et al.	424	489	08-18-98
		6,135,987	10-24-00	Tsai, et al.	604	365	12-22-99
		6,169,058 B1	01-02-01	Le, et al.	507	222	06-05-97
		6,202,751 B1	03-20-01	Chatterji, et al.	166	276	07-28-00
		6,209,646 B1	04-03-01	Reddy, et al.	166	300	04-21-99
		6,214,773 B1	04-10-01	Harris, et al.	507	271	09-29-99
		6,260,622 B1	07-17-01	Blok, et al.	166	305.1	12-23-98
		6,311,773 B1	11-06-01	Todd, et al.	166	280	01-28-00
		6,357,527 B1	03-19-02	Norman, et al.	166	300	05-05-00
		6,364,945 B1	04-02-02	Chatterji, et al.	106	677	12-13-00
		6,390,195 B1	05-21-02	Nguyen, et al.	166	276	10-27-00
		6,422,314 B1	07-23-02	Todd, et al.	166	312	08-01-00
		6,454,003 B1	09-24-02	Chang, et al.	166	270	06-14-00
		6,488,763 B2	12-03-02	Brothers, et al.	106	692	10-05-01
		6,494,263 B2	12-17-02	Todd	166	312	01-09-01
		6,508,305 B1	01-21-03	Brannon, et al.	166	293	09-14-00
		6,527,051 B1	03-04-03	Reddy, et al.	166	300	07-12-02
CG		6,554,071 B1	04-29-03	Reddy, et al.	166	293	07-12-02

EXAMINER George Suchfield	DATE CONSIDERED 5/6/05
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EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.

PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al			
Information Disclosure Citation in an Application		Docket Number 2002-IP-009210U1		Group Art Unit 3692	Filing Date 06/27/2003		
U.S. PATENT DOCUMENTS							
		DOCUMENT NO.	ISSUE/PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
CS		6,569,814 B1	05-27-03	Brady, <i>et al.</i>	507	201	04-20-00
		6,667,279 B1	12-23-03	Hessert, <i>et al.</i>	507	225	11-13-97
		6,681,856 B1	01-27-04	Chatterji, <i>et al.</i>	166	294	05-16-03
		6,686,328 B1	02-03-04	Binder	510	446	07-09-99
		US 2003/0188766A1	10-09-03	Banerjee, <i>et al.</i>	134	7	12-19-02
		US 2004/0055747A1	03-25-04	Lee	166	278	09-20-02
		US 2004/0106525A1	06-03-04	Willbert, <i>et al.</i>	507	200	10-17-03
		US 2004/0138068A1	07-15-04	Rimmer, <i>et al.</i>	507	100	12-19-03
		US 2004/0152601A1	08-05-04	Still, <i>et al.</i>	507	100	10-27-03
CS		US 2004/0152602A1	08-05-04	Boles	507	100	01-15-04
FOREIGN PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION
							Yes No
CS		WO 99/27229	06-03-99	PCT	E21B	43/26	X
		WO 01/87797 A1	11-22-01	PCT	C04B	28/02	X
		WO 03/027431 A2	04-03-03	PCT	E21B	-	X
		WO 03/027431 A3	04-03-03	PCT	E21B	43/26	X
CS		EP 0 510 762 A2	04-16-92	Europe	C11D	17/00	X
EXAMINER George Suchfield					DATE CONSIDERED 5/6/05		
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.							

PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al				
Information Disclosure Citation in an Application		Docket Number 2002-IP-009210U1		Group Art Unit 3672	Filing Date 06/27/2003			
FOREIGN PATENT DOCUMENTS								
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION Yes No	
NON-PATENT DOCUMENTS								
		DOCUMENT (Including Author, Title, Source, and Pertinent Pages)						
69		Cantu, et al, <i>Laboratory and Field Evaluation of a Combined Fluid-Loss-Control Additive and Gel Breaker for Fracturing Fluids</i> , SPE 18211, Society of Petroleum Engineers, 1990						
1		Love, et al, <i>Selectively Placing Many Fractures in Openhole Horizontal Wells Improves Production</i> , SPE 50422, Society of Petroleum Engineers, 1998						
1		McDaniel, et al, <i>Evolving New Stimulation Process Proves Highly Effective in Level 1 Dual-Lateral Completion</i> , SPE 78697, Society of Petroleum Engineers, 2002						
1		Albertsson, et al, <i>Aliphatic Polyesters: Synthesis, Properties and Applications</i> , Advances in Polymer Science, Vol. 157, 2002						
1		Dechy-Cabaret, et al, <i>Controlled Ring-Opening Polymerization of Lactide and Glycolide</i> , American Chemical Society, Chemical Reviews, A-Z, AA-AD, received 2004						
1		Funkhouser, et al, <i>Synthetic Polymer Fracturing Fluid for High-Temperature Applications</i> , SPE 80236, Society of Petroleum Engineers, 2003						
1		<i>Chelating Agents</i> , Encyclopedia of Chemical Technology, Vol. 5 (764-795)						
1		Vichaibun, et al, <i>A New Assay for the Enzymatic Degradation of Polylactic Acid</i> , Short Report, ScienceAsia, Vol. 29, 2003 (pp. 297-300)						
1		Halliburton, <i>SurgiFracSM Service, A Quick and Cost-Effective Method to Help Boost Production From Openhole Horizontal Completions</i> , Halliburton Communications, HO3297, 2002						
1		Halliburton, <i>Cobra FracSM Service, Coiled Tubing Fracturing—Cost-Effective Method for Stimulating Untapped Reserves</i> , HO2319R, Halliburton Energy Services, 2000						
1		Halliburton, <i>CobraJet FracSM Service, Cost-effective Technology That Can Help Reduce Cost Per BOE Produced, Shorten Cycle Time and Reduce Capex</i> , Halliburton Communications						
1		Blauch, et al, <i>Aqueous Tackifier and Methods of Controlling Particulates</i> , Patent Application No. 10/864,061, filed 06-09-04						
69		Blauch, et al, <i>Aqueous-Based Tackifier Fluids and Methods of Use</i> , Patent Application No. 10/864,618, filed 06-09-04						
EXAMINER		George Suchfield				DATE CONSIDERED 5/6/05		
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.								

PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen <i>et al.</i>		
Information Disclosure Citation in an Application 		Docket Number 2002-IP-09210U1		Group Art Unit 3672	Filing Date 06-27-2003	
U.S. PATENT DOCUMENTS						
	DOCUMENT NO.	ISSUE/ PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
69	2,238,671	04-15-41	Woodhouse	166	21	02-09-40
	3,784,585	01-08-74	Schmitt <i>et al.</i>	260	861	10-21-71
	3,828,854	08-13-74	Templeton <i>et al.</i>	166	307	10-30-73
	3,868,998	03-04-75	Lybarger <i>et al.</i>	166	278	05-15-74
	4,169,798	10-02-79	DeMartino	252	8.55R	10-25-77
	4,470,915	09-11-84	Conway	252	8.55R	09-27-82
	4,716,964	01-05-88	Erbstoesser <i>et al.</i>	166	284	12-10-86
	4,809,783	03-07-89	Hollenbeck <i>et al.</i>	166	307	01-14-88
	4,843,118	06-27-89	Lai <i>et al.</i>	524	555	06-19-87
	4,961,466	10-09-90	Himes <i>et al.</i>	166	250	01-23-89
	4,986,354	01-22-91	Cantu <i>et al.</i>	166	279	09-14-88
	5,082,056	01-21-92	Tackett Jr.	166	295	10-16-90
	5,439,055	08-08-95	Card <i>et al.</i>	166	280	03-08-94
	5,460,226	10-24-95	Lawson <i>et al.</i>	166	300	05-18-94
	5,591,700	01-07-97	Harris <i>et al.</i>	507	204	12-22-94
	6,162,766	12-19-00	Muir <i>et al.</i>	507	267	05-29-98
	6,189,615	02-20-01	Sydansk	166	270	12-15-98
	6,242,390	06-05-01	Mitchell <i>et al.</i>	507	211	07-31-98
69	6,387,986	05-04-02	Moradi-Araghi <i>et al.</i>	523	211	06-24-99
FOREIGN PATENT DOCUMENTS						
	DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION Yes No
69	WO 04/038176 A1	05/06/04	United States	E21B	43/27	n/a
NON-PATENT DOCUMENTS						
	DOCUMENT (Including Author, Title, Source, and Pertinent Pages)					
EXAMINER <i>George Suchfield</i>				DATE CONSIDERED <i>5/6/05</i>		
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.						

PTO-1449 Information Disclosure Citation in an Application		Application No. 10/608,291 Docket Number 2002-IP-09210U1		Applicant(s) Philip D. Nguyen <i>et al.</i> Group Art Unit 3072 Filing Date 06-27-2003	
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U.S. PATENT DOCUMENTS

		DOCUMENT NO.	ISSUE/PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
67		6,669,771	12-30-03	Tokiwa <i>et al.</i>	106	162	12-08-02
		6,710,019	03-23-04	Sawdon <i>et al.</i>	507	136	07-16-99
		US 2001/0016562	08-23-01	Muir <i>et al.</i>	507	201	11-29-00
		US 2003/0060374	03-27-03	Cooke Jr.	507	200	09-24-02
		US 2003/0114314	06-19-03	Ballard <i>et al.</i>	507	100	12-19-01
		US 2003/0130133	07-10-03	Vallmer	507	100	12-11-02
		US 2003/0234103	12-25-03	Lee <i>et al.</i>	166	293	06-20-02
		US 2004/0014607	01-22-04	Sinclair <i>et al.</i>	507	200	07-16-02
67		US 2004/0040706	03-04-04	Hossaini <i>et al.</i>	166	278	08-28-02

FOREIGN PATENT DOCUMENTS

		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
							Yes	No
67		WO 04/037946 A1	05-06-04	United States	C09K	7/00		n/a

NON-PATENT DOCUMENTS

		DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	

EXAMINER George Suchfield	DATE CONSIDERED 5/6/05
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Sheet 1 of 1 69

FORM PTO-1449 (Modified) LIST OF PATENTS AND PUBLICATIONS FOR APPLICANT'S INFORMATION DISCLOSURE STATEMENT (Use several sheets if necessary)	ATTY. DOCKET NO. 2002-IP-009210U1	SERIAL NO. 10/608,291
	APPLICANT Philip D. Nguyen, et al	
	FILING DATE 06/27/2003	GROUP 3672

U.S. PATENT DOCUMENTS

EXAMINER INITIAL		Document No.	Date	Name	Class	Subclass	Filing Date if Appropriate
69	AA	6,599,863	07/29/03	Palmer, et al	507	219	
	AB						
	AC						
	AD						
	AE						
	AF						
	AG						
	AH						
	AI						
	AJ						
	AK						

FOREIGN PATENT DOCUMENTS

		Document No.	Date	Country	Class	Subclass	Translation	
							Yes	No
	AL							
	AM							

OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)

AN	
AO	
AP	

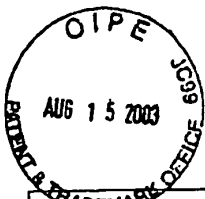
EXAMINER

George Suchfield

DATE CONSIDERED

5/6/05

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Sheet 1 of 1

FORM PTO-1449 (Modified) LIST OF PATENTS AND PUBLICATIONS FOR APPLICANT'S INFORMATION DISCLOSURE STATEMENT (Use several sheets if necessary)	ATTY. DOCKET NO. 2002-IP-009210U1	SERIAL NO. 10/608,291
	APPLICANT Philip D. Nguyen, et al	
	FILING DATE 06/27/03	GROUP <u>3672</u>

U.S. PATENT DOCUMENTS

EXAMINER INITIAL		Document No.	Date	Name	Class	Subclass	Filing Date if Appropriate
<u>09</u>	AA	3,955,993	05/11/76	Curtice, et al	106	662	
	AB	3,948,672	04/06/76	Harnsberger	106	720	
	AC	6,485,947	11/26/02	Rajgarhia, et al	435	139	
	AD	4,526,695	07/02/85	Erbstoesser, et al	507	219	
	AE	6,172,011	01/09/01	Card, et al	507	204	
	AF	5,924,488	07/20/99	Nguyen, et al	166	280	
	AG	6,209,643	04/03/01	Nguyen, et al	166	276	
	AH	6,047,772	04/11/00	Weaver, et al	166	276	
	AI	5,908,073	06/01/99	Nguyen, et al	166	276	
	AJ	5,791,415	08/11/98	Nguyen, et al	166	280	
	AK	4,694,905	09/22/87	Armbruster	166	280	
	AL	4,785,884	11/22/88	Armbruster	166	280	
<u>09</u>	AM	6,328,105	12/11/01	Betzold	166	280	

FOREIGN PATENT DOCUMENTS

		Document No.	Date	Country	Class	Subclass	Translation	
							Yes	No
<u>09</u>	AN	WO 03/027431	04/03/03	United States	E2	4B	X	
	AO							
	AP							
	AQ							
	AR							

OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)

	AS	
	AT	
	AU	

EXAMINER

George Suchfield

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Sheet 1 of 2

FORM PTO-1449 (Modified) LIST OF PATENTS AND PUBLICATIONS FOR APPLICANT'S INFORMATION DISCLOSURE STATEMENT (Use several sheets if necessary)	ATTY. DOCKET NO. 2002-IP-009210U1	SERIAL NO. Unknown <u>10/608291</u>
	APPLICANT Philip D. Nguyen, et al	
	FILING DATE Concurrently Herewith	GROUP Unknown <u>367</u>

U.S. PATENT DOCUMENTS

EXAMINER INITIAL		Document No.	Date	Name	Class	Subclass	Filing Date if Appropriate
<u>GS</u>	AA	4,387,769	06/14/83	Erbstoesser, et al	507	219	
	AB	4,526,695	07/02/85	Erbstoesser, et al	507	219	
	AC	6,172,011	01/09/01	Card, et al	507	204	
	AD	5,924,488	07/20/99	Nguyen, et al	466	280	
	AE	6,209,643	04/03/01	Nguyen, et al	166	276	
	AF	6,047,772	04/11/00	Weaver, et al	166	276	
	AG	5,908,073	06/01/99	Nguyen, et al	166	276	
	AH	5,791,415	08/11/98	Nguyen, et al	166	280	
	AI	4,694,905	09/22/87	Armbruster	166	280	
	AJ	4,785,884	11/22/88	Armbruster	166	280	
<u>GS</u>	AK	4,986,355	01/22/91	Casad, et al	166	295	

FOREIGN PATENT DOCUMENTS

		Document No.	Date	Country	Class	Subclass	Translation	
							Yes	No
	AL							
	AM							

OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)

<u>GS</u>	AN	"Poly(phenyllactide): Synthesis, Characterization, and Hydrolytic Degradation" published in Biomacromolecules, Vol. 2, No. 3, 2001, pages 658-663 by Tara L. Simmons and Gregory L. Baker.
<u>GS</u>	AO	"Synthesis and Properties of Polymers Derived from Substituted Lactic Acids" published in 2001 American Chemical Society, Chapter 12, pages 147-159 by Mao Yin, Tara L. Simmons and Gregory L. Baker.
<u>GS</u>	AP	"Preparation and Characterization of Substituted Poly lactides" published in 199 American Chemical Society, Volume 32, Number 23, pages 7711-7718 by Mao Yin and Gregory L. Baker.

EXAMINER

George Suchfield

DATE CONSIDERED

5/6/05

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

FORM PTO-1449 (Modified) LIST OF PATENTS AND PUBLICATIONS FOR APPLICANT'S INFORMATION DISCLOSURE STATEMENT (Use several sheets if necessary)	ATTY. DOCKET NO. 2002-IP-009210U1	SERIAL NO. Unknown <u>10/604291</u>
	APPLICANT Philip D. Nguyen, et al	
	FILING DATE Concurrently Herewith	GROUP Unknown <u>3672</u>

U.S. PATENT DOCUMENTS

EXAMINER INITIAL		Document No.	Date	Name	Class	Subclass	Filing Date if Appropriate
<u>69</u>	AA	4,715,967	12/29/87	Bellis, et al	252	8.551	
	AB	4,886,354	12/12/89	Welch, et al	356	70	
	AC	4,986,353	01/22/91	Clark, et al	166	279	
	AD	4,957,165	09/18/90	Cantu, et al	166	295	
	AE	4,848,467	07/18/89	Cantu, et al	166	281	
	AF	3,960,736	06/01/76	Free, et al	252	8.55	
<u>69</u>	AG	5,216,050	06/01/93	Sinclair	524	108	
	AH	6,323,307	11/27/01	Bigg, et al	528	354	
	AI						
	AJ						
	AK						

FOREIGN PATENT DOCUMENTS

	Document No.	Date	Country	Class	Subclass	Translation	
						Yes	No
AL							
AM							

OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)

AN							
AO							
AP							

EXAMINER

George Suchfield

DATE CONSIDERED

5/6/05

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Search Notes



Application No.

10/608,291

Examiner

George Suchfield

Applicant(s)

NGUYEN ET AL.

Art Unit

3672

SEARCHED

Class	Subclass	Date	Examiner
166	276		
	276		
	280.1		
	280.2		
	281		
	295		
	300		
	308.1		
	308.2		
507	209		
	211		
	219		
	220		
	260	5/5/05	GS

INTERFERENCE SEARCHED

Class	Subclass	Date	Examiner

SEARCH NOTES (INCLUDING SEARCH STRATEGY)

	DATE	EXMR
EAST-BRS	5/5/05	GS
S.N. 10/608,373 refs cited	5/5/05	GS

Search Notes (continued)


Application No.

10/608,291

Examiner

George Suchfield

Applicant(s)

NGUYEN ET AL.

Art Unit

3672

SEARCHED

Class	Subclass	Date	Examiner
509	273		
	924		
	906		
523	130		
	131	5/6/05	GS

INTERFERENCE SEARCHED

Class	Subclass	Date	Examiner

**SEARCH NOTES
(INCLUDING SEARCH STRATEGY)**

	DATE	EXMR

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L2	81	(proppant\$1 or propping) WITH void\$1	US-PGPUB; USPAT; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2005/05/05 10:21
S1	1	"20040261995".pn.	US-PGPUB; USPAT	OR	OFF	2005/05/05 07:18
S2	4	("20040261995" "20040261996" "20040261999" "20040261993").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 07:37
S3	1	("20040231845").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 07:52
S4	3	("6114410" "6059034" "20030060374").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 07:48
S5	19	("2238671" "3784585" "3828854" "3868998" "4169798" "4470915" "4716964" "4809783" "4843118" "4961466" "4986354" "5082056" "5439055" "5460226" "5591700" "6162766" "6189615" "6242390" "6387986").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 07:55
S6	1	("6599863").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 07:57
S7	13	("6439309" "4817721" "5142023" "5247059" "5359026" "5475080" "5484881" "5536807" "5594095" "5839510" "5849401" "6326458" "6488091").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 08:00
S8	13	("3955993" "3948672" "6485947" "4526695" "6172011" "5924488" "6209643" "6047772" "5908073" "5791415" "4694905" "4785884" "6328105").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 08:03
S9	19	("4387769" "4526695" "6172011" "5924488" "6209643" "6047772" "5908073" "5791415" "4694905" "4785884" "4986355" "4715967" "4886354" "4986353" "4957165" "4848467" "3960736" "5216050" "6323307").PN.	US-PGPUB; USPAT	OR	OFF	2005/05/05 08:04
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S12	1	"3818991".pn.	US-PGPUB; USPAT	OR	OFF	2005/05/05 08:35

S13	1	S11 and S12	US-PGPUB; USPAT	OR	OFF	2005/05/05 08:34
S14	1	"4210455".pn.	US-PGPUB; USPAT	OR	OFF	2005/05/05 08:36
S15	1	"4526695".pn.	US-PGPUB; USPAT	OR	OFF	2005/05/05 08:36
S16	81	(proppant\$1 or propping) WITH void\$1	US-PGPUB; USPAT; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2005/05/05 08:38
S17	101	(proppant\$1 or propping) WITH (degrade\$1 or degrading or degradation)	US-PGPUB; USPAT; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2005/05/05 08:39
S18	7	S16 and S17	US-PGPUB; USPAT; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2005/05/05 08:38



Ifw

Practitioner's Docket No. 2002-IP-009210U1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of _____
Inventor(s)

for _____
Title of Invention

OR

In re application of: Philip D. Nguyen, et al

Application No.: 0 10 / 608,291

Group Art Unit:

Filed: 06/27/2003

Examiner:

For: Compositions and Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean Well

Mail Stop Amendment

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
WITHIN THREE MONTHS OF FILING OR
BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))**

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

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☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10 *

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Date: 3/15/05

Tammy Knight
Signature

Tammy Knight

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 1 of 3)

NOTE: 37 C.F.R. 1.99(b):

(1) Each U.S. patent listed in an information disclosure statement must be identified by inventor, patent number, and issue date.

(2) Each U.S. patent application publication listed in an information disclosure statement shall be identified by applicant, patent application publication number, and publication date.

(3) Each U.S. application listed in an information disclosure statement must be identified by the inventor, application number, and filing date.

(4) Each foreign patent or published foreign patent application listed in an information disclosure statement must be identified by the country or patent office which issued the patent or published the application, an appropriate document number, and the publication date indicated on the patent or published application.

(5) Each publication listed in an information disclosure statement must be identified by publisher, author (if any), title, relevant pages of the publication, date, and place of publication.

WARNING: No extension of time can be had under 37 C.F.R. § 1.136 (a) or (b) for filing an IDS. 37 C.F.R. § 1.97(f).

NOTE: The "filing date of a national application" under 37 C.F.R. § 1.97(b) has two possible meanings. Where the filing is a direct one to the United States Patent & Trademark Office, the filing is defined in 37 C.F.R. § 1.53(b) as "the date on which: (1) A specification containing a description pursuant to § 1.71 and at least one claim pursuant to § 1.75; and (2) any drawing required by § 1.81(a), are filed in the Patent and Trademark Office in the name of the actual inventor or inventors as required by § 1.41." 37 C.F.R. § 1.97(b)(1). On the other hand, an international application that enters the national stage occurs when the applicant has filed the documents and fees required by 35 U.S.C. § 371(c) within the periods set forth in § 1.494 or § 1.495. 35 U.S.C. § 371(c) requires the filing of the following: (1) the basic national fee; (2) a copy of the international application, unless already sent by the International Bureau, and optionally an English translation if filed in another language; and, also optionally (3) amendments under PCT Article 18, with a translation into English if made in another language; (4) an oath or declaration; and (5) a translation into English of any annexes to the international preliminary examination report, if such annexes were made in another language. The optional items must be submitted later, with surcharges. 37 C.F.R. § 1.97(b)(2).

IDENTIFICATION OF TIME OF FILING THE ACCOMPANYING INFORMATION DISCLOSURE STATEMENT

The information disclosure statement submitted herewith is being filed within three months of the filing date of the application or date of entry into the national stage of an international application or before the mailing date of a first Office action on the merits, whichever event occurs last. 37 C.F.R. § 1.97(b).

NOTE: "No certification or fee is due when the filing is made within the above time period. It is advisable to ensure that no Office action has been mailed if the disclosure statement is delayed until after three months from filing."

NOTE: "An information disclosure statement will be considered to have been filed on the day it was received in the Office, or on an earlier date of a mailing if accompanied by a properly executed certificate of mailing under 37 C.F.R. 1.8, or Express Mail certificate under 37 C.F.R. 1.10. An Office action is mailed on the date indicated in the Office action." Notice of April 20, 1992 (1138 O.G. 37-41, 39). See also § 608, M.P.E.P., 8th Edition.

NOTE: "The term 'national application' includes continuing applications (continuations, divisions, continuations-in-part) so three-months will be measured from the actual filing date of an application as opposed [sic] to the effective date of a continuing application." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [E-3]—page 2 of 3)

NOTE: "An action on the merits means an action which treats the patentability of the claims in an application, as opposed to only formal or procedural requirements. An action on the merits would, for example, contain a rejection or indication of allowability of a claim or claims rather than just a restriction requirements (37 C.F.R. 1.142) or just a requirement for additional fees to have a claim considered (37 C.F.R. 1.16(d)). Thus, if an application was filed on Jan. 1 and the first Office action on the merits was not mailed until six months later on July 1, the examiner would be required to consider any proper information disclosure statement filed prior to July 1." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

WARNING: "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1992 (1141 O.G. 63). But see § 103(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(d) and in a request for continued examination (RCE) under § 1.114.

Reg. No.: 28,626

Tel. No.: (580) 251-3125

Customer No.:


SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

P.O. Box 1431

P.O. Address

Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [8-3]—page 3 of 3)



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Philip D. Nguyen, et al)	
)	Art Unit: Unknown
Serial No.:	10/608,291)	
)	
Filed:	06/27/2003)	Examiner: Unknown
)	
For:	Compositions and Methods)	
	For Improving Proppant)	
	Pack Permeability and)	
	Fracture Conductivity in a)	
	Subterranean Well)	

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

COMMISSIONER FOR PATENTS
Alexandria, VA 22313-1450

SIR:

The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

U. S. PATENTS

U.S. Patent Number 6,763,888 B1 issued 07/20/04 to Ralph Edmund Harris, et al;

U.S. Patent Application Publication Number 2004/0261993 A1 published 12/30/04 by Philip D. Nguyen (S/N 10/608,319, Ref. No. 2003-IP-010077U1, filed 06/27/03);

U.S. Patent Application Publication Number 2004/0261995 A1 published 12/30/04 by Philip D. Nguyen, et al (S/N 10/608,291, Ref. No. 2002-IP-009210U1, filed 06/27/03);

U.S. Patent Application Publication Number 2004/0261996 A1 published 12/30/04 by Trinidad Munoz, Jr., et al (S/N 10/609,031, Ref. No. 2002-IP-009052U1, filed 06/27/03); and

U.S. Patent Application Publication Number 2004/0261999 A1 published 12/30/04 by Philip D. Nguyen (S/N 10/608,373, Ref. No. 2003-IP-010077U2, filed 06/27/03).

FOREIGN PATENTS

European Patent Number 0 879 935 A3 published 02/10/99 by Jim D. Weaver, et al.

PAPERS/OTHER

None.

BROCHURES

None.

Copies of the aforementioned non-patent references and Form PTO-1449 are submitted herewith.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Robert A. Kent", written over a horizontal line.

Robert A. Kent
Registration No. 28,626
Halliburton Energy Services
P. O. Box 1431
Duncan, OK 73536-0440
580-251-3125



PTO-1449 Information Disclosure Citation in an Application	Application No. 10/608,291	Applicant(s) Philip D. Nguyen, et al	
	Docket Number 2002-IP-009210U1	Group Art Unit	Filing Date 06/27/2003

U.S. PATENT DOCUMENTS

		6,763,888 B1	07/20/04	Harris, et al	166	305.1	03/20/00
		US 2004/0261993A1 (US Pat. App. Ser. No. 10/608,319)	12/30/04	Nguyen (Ref. No. 2003-IP-010077U1)	166	276	06/27/03
		US 2004/0261995A1 (US Pat. App. Ser. No. 10/608,291)	12/30/04	Nguyen, et al (Ref. No. 2002-IP-009210U1)	166	279	06/27/03
		US 2004/0261996A1 (US Pat. App. Ser. No. 10/609,031)	12/30/04	Munoz, Jr., et al (Ref. No. 2002-IP-009052U1)	166	279	06/27/03
		US 2004/0261999A1 (US Pat. App. Ser. No. 10/608,373)	12/30/04	Nguyen (Ref. No. 2003-IP-010077U2)	166	292	06/27/03

FOREIGN PATENT DOCUMENTS

		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
							Yes	No
		EP 0 879 935 A3	10-02-99	Europe	E21B	43/26	X	

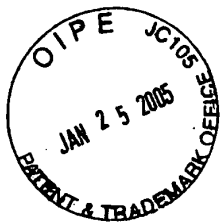
EXAMINER

DATE CONSIDERED

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.

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JFW



Practitioner's Docket No. 2002-IP-009210U1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of _____
Inventor(s)

for _____
Title of Invention

OR

In re application of: Philip D. Nguyen, et al

Application No.: 0 10/608,291

Group Art Unit:

Filed: 06/27/2003

Examiner:

For: Compositions and Methods for Improving Proppant Pack Permeability
And Fracture Conductivity in a Subterranean Well

~~Mail Stop Amendment~~

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
WITHIN THREE MONTHS OF FILING OR
BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))**

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

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☒ deposited with the United States Postal Service in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450

37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10 *

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Mailing Label No. _____ (mandatory)

TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 1/21/05

Tammy Knight
Signature

Tammy Knight

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.8(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 1 of 3)

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NOTE: 37 C.F.R. 1.98(b):

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(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 2 of 3)

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NOTE: "An action on the merits means an action which treats the patentability of the claims in an application, as opposed to only formal or procedural requirements. An action on the merits would, for example, contain a rejection or indication of allowability of a claim or claims rather than just a restriction requirements (37 C.F.R. 1.142) or just a requirement for additional fees to have a claim considered (37 C.F.R. 1.16(d)). Thus, if an application was filed on Jan. 1 and the first Office action on the merits was not mailed until six months later on July 1, the examiner would be required to consider any proper information disclosure statement filed prior to July 1." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

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Reg. No.: 28,626

Tel. No.: (580) 251-3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

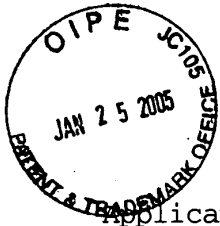
(type or print name of practitioner)

P.O. Box 1431

P.O. Address

Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 3 of 3)



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Philip D. Nguyen, et al)
Serial No.: 10/608,291) Art Unit: Unknown
Filed: 06/27/2003) Examiner: Unknown
For: Compositions and Methods)
For Improving Proppant)
Pack Permeability and)
Fracture Conductivity)
In a Subterranean Well)

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

COMMISSIONER FOR PATENTS
Alexandria, VA 22313-1450

SIR:

The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

U. S. PATENTS

U.S. Patent Number 4,817,721 issued 04/04/89 to Kenneth W. Pober;
U.S. Patent Number 5,142,023 issued 08/25/92 to Patrick R. Gruber, et al;
U.S. Patent Number 5,247,059 issued 09/21/93 to Patrick R. Gruber, et al;
U.S. Patent Number 5,359,026 issued 10/25/94 to Patrick R. Gruber;
U.S. Patent Number 5,475,080 issued 12/12/95 to Patrick R. Gruber, et al;
U.S. Patent Number 5,484,881 issued 01/16/96 to Patrick R. Gruber, et al;
U.S. Patent Number 5,536,807 issued 07/16/96 to Patrick R. Gruber, et al;

U.S. Patent Number 5,594,095 issued 01/14/97 to Patrick R. Gruber, et al;

U.S. Patent Number 5,839,510 issued 11/24/98 to Jim D. Weaver, et al;

U.S. Patent Number 5,849,401 issued 12/15/98 to Ali Zakareya El-Afandi, et al;

U.S. Patent Number 6,326,458 B1 issued 12/04/01 to Patrick Richard, Gruber, et al;

U.S. Patent Number 6,439,309 B1 issued 08/27/02 to Ronald M. Matherly, et al;

U.S. Patent Number 6,488,091 B1 issued 12/03/02 to Jim D. Weaver, et al;

U.S. Patent Application Number 10/947,427 filed 09/20/04, *Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean Well* by Matthew E. Blauch, et al, (Ref. No. 2002-IP-009210U1P1);

U.S. Patent Application, Serial No. Unassigned and filing date currently unknown, *Compositions and Methods for Improving Fracture Conductivity in a Subterranean Well* by Bradley L. Todd, et al, (Ref. No. 2002-IP-009210U1P2); and

U.S. Patent Application, Serial No. Unassigned and filing date currently unknown, *Compositions and Methods for Improving Fracture Conductivity in a Subterranean Well* by Bradley L. Todd, et al, (Ref. No. 2002-IP-009210U1P3).

FOREIGN PATENTS

Int'l Patent Publication No. WO 93/15127 A1 published 08/05/93 by Patrick R. Gruber, et al;

Int'l Patent Publication No. WO 94/07949 A1 published 04/14/94 by Patrick Richard Gruber, et al;

Int'l Patent Publication No. WO 94/08078 A1 published 04/14/94 by Patrick Richard

Gruber, et al;

Int'l Patent Publication No. WO 94/08090 A1 published 04/14/94 by Patrick Richard

Gruber, et al;

Int'l Patent Publication No. WO 95/09879 A1 published 04/13/95 by Patrick Richard

Gruber, et al; and

Int'l Patent Publication No. WO 97/11845 A1 published 04/03/97 by Ali Zakareya El-Afandi.

PAPERS/OTHER

None.

BROCHURES

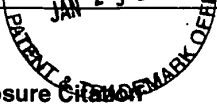
None.

Copies of the aforementioned non-patent references and Form PTO-1449 are submitted herewith.

Respectfully submitted,



Robert A. Kent
Registration No. 28,626
Halliburton Energy Services
P. O. Box 1431
Duncan, OK 73536-0440
580-251-3125



PTO-1449 Information Disclosure Statement in an Application		Application No. 10/608,291	Applicant(s): PHILIP D. NGUYEN, ET AL	
Docket Number 2002-IP-009210U1		Group Art Unit	Filing Date 06/27/2003	

U.S. PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE
1.		4,817,721	04/04/89	Pober	166	295	12/14/87
2.		5,142,023	08/25/92	Gruber, et al	528	354	01/24/92
3.		5,247,059	09/21/93	Gruber, et al	528	354	08/24/92
4.		5,359,026	10/25/94	Gruber	528	354	07/30/93
5.		5,475,080	12/12/95	Gruber, et al	528	354	03/22/93
6.		5,484,881	01/16/96	Gruber, et al	528	354	08/23/93
7.		5,536,807	07/16/96	Gruber, et al	528	354	08/23/93
8.		5,594,095	01/14/97	Gruber, et al	528	354	07/27/94
9.		5,839,510	11/24/98	Weaver, et al	166	276	01/14/97
10.		5,849,401	12/15/98	El-Afandi, et al	428	215	05/03/96
11.		6,326,458 B1	12/04/01	Gruber, et al	528	354	10/07/93
12.		6,439,309 B1	08/27/02	Matherly, et al	166	276	12/13/00
13.		6,488,091B1	12/03/02	Weaver, et al	166	300	06/11/01

FOREIGN PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION
							YES NO
A.		WO 93/15127 A1	08/05/93	PCT	C08G	63/06	X
B.		WO 94/07949 A1	04/14/94	PCT	C08K	11/00	X
C.		WO 94/08078 A1	04/14/94	PCT	D01F	6/62	X
D.		WO 94/08090 A1	04/14/94	PCT	D21H	19/28	X

NON-PATENT DOCUMENTS	
DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE

EXAMINER	DATE CONSIDERED
----------	-----------------

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.

PTO-1449 Information Disclosure Citation in an Application		Application No. 10/608,291		Applicant(s): PHILIP D. NGUYEN, ET AL			
		Docket Number 2002-IP-009210U1		Group Art Unit		Filing Date 06/27/2003	

U.S. PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	NAME	CLASS	SUBCLASS	FILING DATE
	14.	US Patent App. No. 10/947,427	-	Blauch, et al (Ref. No. 2002- IP-009210U1P1)	-	-	09/20/04
	15.	US Patent App. (Serial No. Unassigned)	-	Todd, et al (Ref. No. 2002- IP-009210U1P2)	-	-	-
	16.	US Patent App. (Serial No. Unassigned)		Todd, et al (Ref. No. 2002- IP-009210U1P3)	-	-	-

FOREIGN PATENT DOCUMENTS								
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
	E.	WO 95/09879 A1	04/13/95	PCT	C08G	63/08	X	
	F.	WO 97/11845 A1	04/03/97	PCT	B32B	27/08	X	

NON-PATENT DOCUMENTS	
DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	DATE

EXAMINER	DATE CONSIDERED
----------	-----------------

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.

162

Practitioner's Docket No. 2002-IP-009210U1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of _____
Inventor(s)

for _____
Title of Invention

OR

In re application of: Philip D. Nguyen, et al

Application No.: 0 10 / 608,291

Group Art Unit:

Filed: 06/27/2003

Examiner:

For: Compositions and Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean Well

Mail Stop Amendment

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
WITHIN THREE MONTHS OF FILING OR
BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))**

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*

(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

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37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10 *

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TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 12/14/04

Tammy Knight
Signature

Tammy Knight

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 1 of 3)

NOTE: 37 C.F.R. 1.98(b):

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(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [8-3]—page 2 of 3)

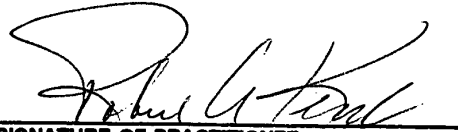
NOTE: "An action on the merits means an action which treats the patentability of the claims in an application, as opposed to only formal or procedural requirements. An action on the merits would, for example, contain a rejection or indication of allowability of a claim or claims rather than just a restriction requirements (37 C.F.R. 1.142) or just a requirement for additional fees to have a claim considered (37 C.F.R. 1.16(d)). Thus, if an application was filed on Jan. 1 and the first Office action on the merits was not mailed until six months later on July 1, the examiner would be required to consider any proper information disclosure statement filed prior to July 1." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

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Reg. No.: 28,626

Tel. No.: (580) 251-3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

P.O. Box 1431

P.O. Address

Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 3 of 3)



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Philip D. Nguyen)	
)	Art Unit: Unknown
Serial No.:	10/608,291)	
)	
Filed:	06/27/2003)	Examiner: Unknown
)	
For:	Compositions and Methods)	
	For Improving Proppant)	
	Pack Permeability and)	
	Fracture Conductivity)	
	In a Subterranean Well)	

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

COMMISSIONER FOR PATENTS
Alexandria, VA 22313-1450

SIR:

The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

U.S. PATENTS

U.S. Publication Number 2004/0231845A1 published 11/25/04 by Claude E. Cooke, Jr.

FOREIGN PATENTS

None.

PAPERS/OTHER

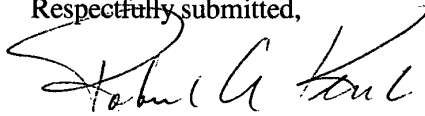
None.

BROCHURES

None.

Copies of the aforementioned non-patent references and Form PTO-1449 are submitted
herewith.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Robert A. Kent", written over the typed name.

Robert A. Kent
Registration No. 28,626
Halliburton Energy Services
P. O. Box 1431
Duncan, OK 73536-0440
580-251-3125

Practitioner's Docket No. 2002-IP-009210U1

PATENT



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of _____
Inventor(s)

for _____
Title of invention

OR

In re application of: Philip D. Nguyen, et al

Application No.: 0 10/608,291

Group Art Unit:

Filed: 06/27/2003

Examiner:

For: Compositions and Methods for Improving Proppant Pack Permeability
And Fracture Conductivity In a Subterranean Well

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
WITHIN THREE MONTHS OF FILING OR
BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))**

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

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37 C.F.R. § 1.10 *

☐ as "Express Mail Post Office to Addressee"

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TRANSMISSION

☐ facsimile transmitted to the Patent and Trademark Office, (703) _____

Date: 12/8/04

Signature

Tammy Knight

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.8(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [8-3]—page 1 of 3)

NOTE: 37 C.F.R. 1.98(b):

- (1) Each U.S. patent listed in an information disclosure statement must be identified by inventor, patent number, and issue date.
- (2) Each U.S. patent application publication listed in an information disclosure statement shall be identified by applicant, patent application publication number, and publication date.
- (3) Each U.S. application listed in an information disclosure statement must be identified by the inventor, application number, and filing date.
- (4) Each foreign patent or published foreign patent application listed in an information disclosure statement must be identified by the country or patent office which issued the patent or published the application, an appropriate document number, and the publication date indicated on the patent or published application.
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(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [8-3]—page 2 of 3)

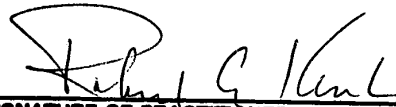
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Reg. No.: 28,626

Tel. No.: (580) 251-3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

(type or print name of practitioner)

P.O. Box 1431

P.O.*Address

Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [6-3]—page 3 of 3)



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Philip D. Nguyen, et al)
Serial No.: 10/608,291) Art Unit: Unknown
Filed: 06/27/2003) Examiner: Unknown
For: Compositions and Methods)
For Improving Proppant)
Pack Permeability and)
Fracture Conductivity)
In a Subterranean Well)

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

COMMISSIONER FOR PATENTS
Alexandria, VA 22313-1450

SIR:

The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

Each item of information contained in this supplemental information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three (3) months prior to the filing of the information disclosure statement.

U. S. PATENTS

U.S. Patent Number 6,059,034 A issued 05/09/00 to Allan R. Rickards, et al;

U.S. Patent Number 6,114,410 A issued 09/05/00 to Donald E. Betzold; and

U.S. Publication Number 2003/0060374 A1 published 03/27/03 by Claude E. Cooke, Jr.

FOREIGN PATENTS

PCT Application No. WO 02/012674 A1 published 02/14/2002 by Hugh Bourne, et al;
European Patent Number 0 879 935 A2 published 11/25/1998 by Jim D. Weaver, et al;
and
UK Patent Number GB 2 348 907 A published 10/18/2000 by Allan R. Rickards, et al.

OTHER MATERIALS

Foreign communication from a related counterpart (International Application
PCT/GB2004/002719, filed 06/24/2004) mailing dated 10/18/2004 and Written Opinion.

Copies of the aforementioned non-patent references and Form PTO-1449 are submitted
herewith.

Respectfully submitted,



Robert A. Kent

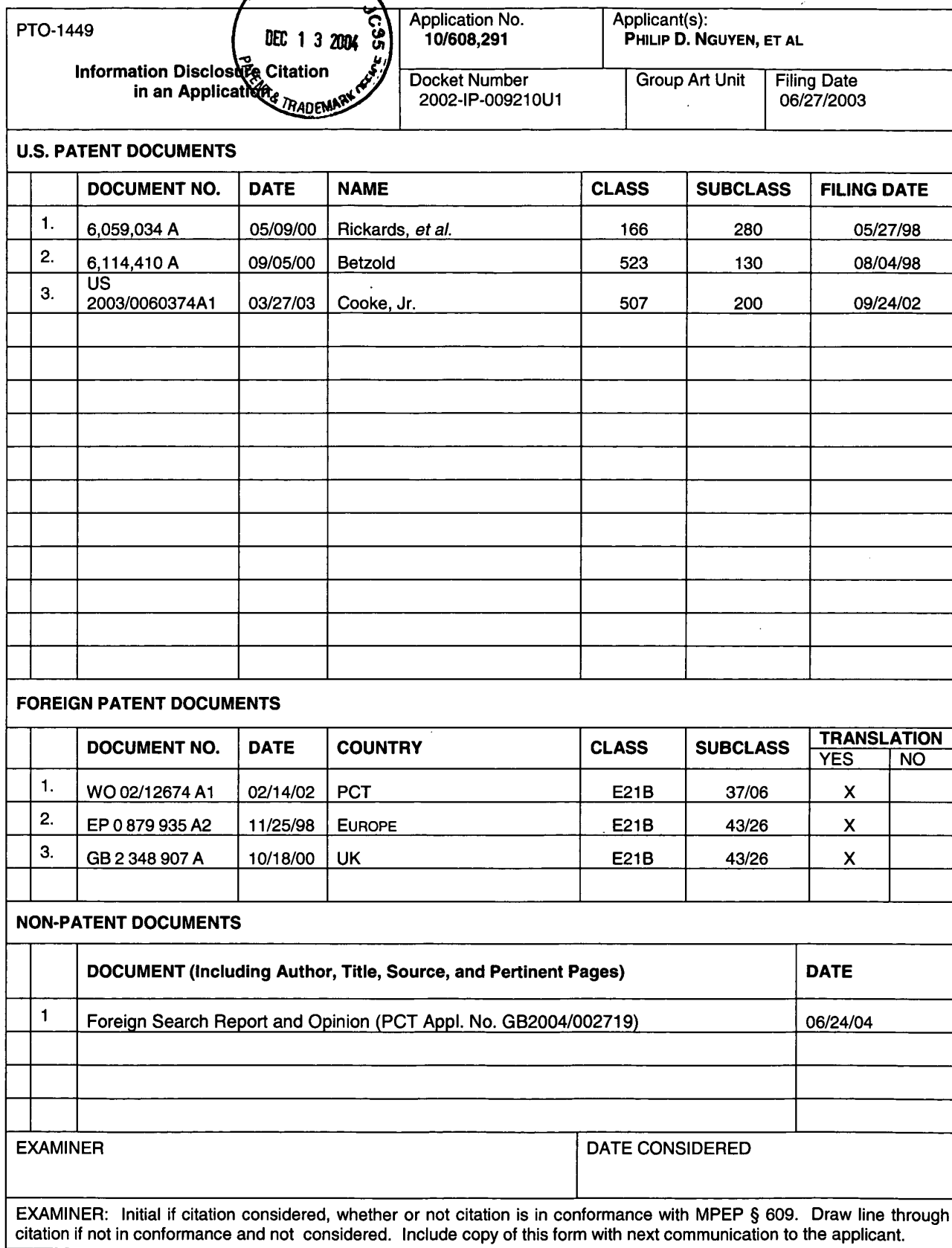
Registration No. 28,626

Halliburton Energy Services

P. O. Box 1431

Duncan, OK 73536-0440

580-251-3125



Practitioner's Docket No. 2002-IP-009210U1

JFW
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of _____
Inventor(s)

for _____
Title of invention

OR

In re application of: PhilipDD. Nguyen, et al

Application No.: 10 / 608,291

Group Art Unit:

Filed: 06/27/03

Examiner:

For: Compositions and Methods for Improving Proppant Pack Permeability
and Fracture Conductivity in a Subterranean Well

Commissioner for Patents

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BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))**

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I hereby certify that, on the date shown below, this correspondence is being:

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Box 1450, Alexandria, VA 22313-1450

37 C.F.R. § 1.8(a)

☒ with sufficient postage as first class mail.

37 C.F.R. § 1.10 *

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TRANSMISSION

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Tammy Knight
Signature

Tammy Knight

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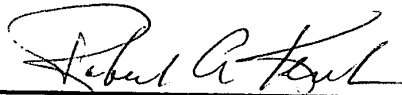
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(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 3 of 3)



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Philip D. Nguyen, et al)	
)	Art Unit: Unknown
Serial No.:	10/608,291)	
)	
Filed:	06/27/2003)	Examiner: Unknown
)	
For:	Compositions and Methods)	
	For Improving Proppant)	
	Pack Permeability and)	
	Fracture Conductivity in)	
	A Subterranean Well)	

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

COMMISSIONER FOR PATENTS
Alexandria, VA 22313-1450

SIR:

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U. S. PATENTS

U.S. Patent Number 2,703,316 issued 03/01/55 to Bentley J. Palmer;
U.S. Patent Number 3,272,650 issued 09/13/66 to Russell L. MacVittie;
U.S. Patent Number 3,819,525 issued 06/25/74 to David L. Hattenbrun;
U.S. Patent Number 3,912,692 issued 10/14/75 to Donald James Casey, et al;
U.S. Patent Number 4,172,066 issued 10/23/79 to Maurice L. Zweigle, et al;
U.S. Patent Number 4,460,052 issued 07/17/84 to Judith Gockel;
U.S. Patent Number 4,498,995 issued 02/12/85 to Judith Gockel;

U.S. Patent Number 4,797,262 issued 01/10/89 to Thomas S. Dewitz;
U.S. Patent Number 5,249,628 issued 10/05/93 to Jim B. Surjaatmadja;
U.S. Patent Number 5,295,542 issued 03/22/94 to R. Clay Cole, et al;
U.S. Patent Number 5,325,923 issued 07/05/94 to Jim B. Surjaatmadja, et al;
U.S. Patent Number 5,330,005 issued 07/19/94 to Roger J. Card, et al;
U.S. Patent Number 5,360,068 issued 11/01/94 to Eve S. Sprunt, et al;
U.S. Patent Number 5,363,916 issued 11/15/94 to Ronald E. Himes, et al;
U.S. Patent Number 5,373,901 issued 12/20/94 to Lewis R. Norman, et al;
U.S. Patent Number 5,386,874 issued 02/07/95 to Steven B. Laramay, et al;
U.S. Patent Number 5,396,957 issued 03/14/95 to Jim B. Surjaatmadja, et al;
U.S. Patent Number 5,402,846 issued 04/04/95 to Alfred R. Jennings, Jr., et al;
U.S. Patent Number 5,464,060 issued 11/07/95 to Arthur H. Hale, et al;
U.S. Patent Number 5,497,830 issued 03/12/96 to Joel L. Boles, et al;
U.S. Patent Number 5,499,678 issued 03/19/96 to Jim B. Surjaatmadja, et al;
U.S. Patent Number 5,505,787 issued 04/09/96 to Kyouichi Yamaguchi;
U.S. Patent Number 5,512,071 issued 04/30/96 to Benny S. Yam, et al;
U.S. Patent Number 5,604,186 issued 02/18/97 to Charles V. Hunt, et al;
U.S. Patent Number 5,670,473 issued 09/23/97 to William H. Scepauski;
U.S. Patent Number 5,698,322 issued 12/16/97 to Fu-Jya Tsai, et al;
U.S. Patent Number 5,765,642 issued 06/16/98 to Jim B. Surjaatmadja;
U.S. Patent Number 5,833,000 issued 11/10/98 to Jim D. Weaver, et al;

U.S. Patent Number 5,853,048 issued 12/29/98 to Jim D. Weaver, et al;
U.S. Patent Number 5,893,416 issued 04/13/99 to Peter Arne Read;
U.S. Patent Number 5,964,291 issued 10/12/99 to Hugh M. Bourne, et al;
U.S. Patent Number 6,004,400 issued 12/21/99 to Phillip W. Bishop, et al;
U.S. Patent Number 6,024,170 issued 02/15/00 to Michael A. McCabe, et al;
U.S. Patent Number 6,028,113 issued 02/22/00 to William H. Scepanski;
U.S. Patent Number 6,123,965 issued 09/26/00 to Jules S. Jacob, et al;
U.S. Patent Number 6,135,987 issued 10/24/00 to Fu-Jya Daniel Tsai, et al;
U.S. Patent Number 6,169,058 B1 issued 01/02/01 to Hoang V. Le, et al;
U.S. Patent Number 6,202,751 B1 issued 03/20/01 to Jiten Chatterji, et al;
U.S. Patent Number 6,209,646 B1 issued 04/03/01 to Baireddy R. Reddy, et al;
U.S. Patent Number 6,214,773 B1 issued 04/10/01 to Phillip C. Harris, et al;
U.S. Patent Number 6,260,622 B1 issued 07/17/01 to Reinoud Hendrik Jurgen Blok, et al;
U.S. Patent Number 6,311,773 B1 issued 11/06/01 to Bradley L. Todd, et al;
U.S. Patent Number 6,357,527 B1 issued 03/19/02 to Lewis R. Norman, et al;
U.S. Patent Number 6,364,945 B1 issued 04/02/02 to Jiten Chatterji, et al;
U.S. Patent Number 6,390,195 B1 issued 05/21/02 to Philip D. Nguyen, et al;
U.S. Patent Number 6,422,314 B1 issued 07/23/02 to Bradley L. Todd, et al;
U.S. Patent Number 6,454,003 B1 issued 09/24/02 to Kin-Tai Chang, et al;
ia, et al;

U.S. Patent Number 6,488,763 B2 issued 12/03/02 to Lance E. Brothers, et al;
U.S. Patent Number 6,494,263 B2 issued 12/17/02 to Bradley L. Todd;
U.S. Patent Number 6,508,305 B1 issued 01/21/03 to Harold D. Brannon, et al;
U.S. Patent Number 6,527,051 B1 issued 03/04/03 to Baireddy R. Reddy, et al;
U.S. Patent Number 6,554,071 B1 issued 04/29/03 to Baireddy R. Reddy, et al;
U.S. Patent Number 6,569,814 B1 issued 05/27/03 to Mark E. Brady, et al;
U.S. Patent Number 6,667,279 B1 issued 12/23/03 to James E. Hessert, et al;
U.S. Patent Number 6,681,856 B1 issued 01/27/04 to Jiten Chatterji, et al;
U.S. Patent Number 6,686,328 B1 issued 02/03/04 to Christopher James Binder;
U.S. Publication Number 2003/0188766 A1 published 10/09/03 by Souvik Banerjee, et al;
U.S. Publication Number 2004/0055747 A1 published 03/25/04 by Li-Jien Lee;
U.S. Publication Number 2004/0106525 A1 published 06/03/04 by Dean Willberg, et al;
U.S. Publication Number 2004/0138068 A1 published 07/15/04 by Brett Rimmer, et al;
U.S. Publication Number 2004/0152601 A1 published 08/05/04 by John W. Still, et al;
U.S. Publication Number 2004/0152602 A1 published 08/05/04 Joel Lynn Boles.

FOREIGN PATENTS

Int'l Publication Number WO 99/27229 A1 published 06/03/99 by Allan R. Rickards, et al;
Int'l Publication Number WO 01/87797 A1 published 11/22/01 by Samuel Danican, et al;

Int'l Publication Number WO 03/027431 A2 published 04/03/03 by Claude E. Cooke, Jr.;
Int'l Publication Number WO 03/027431 A3 published 04/03/03 by Claude E. Cooke, Jr.;
European Patent Number 0 510 762 A2 published 10/28/92 by Mark Philip Houghton, et al.

PAPERS/OTHER

Laboratory and Field Evaluation of a Combined Fluid-Loss-Control Additive and Gel Breaker for Fracturing Fluids, SPE 18211, published 1990 Society of Petroleum Engineers by Lisa A. Cantu, et al;
Selectively Placing Many Fractures in Openhole Horizontal Wells Improves Production, SPE 50422, published 1998 Society of Petroleum Engineers by T. G. Love, et al;
Evolving New Stimulation Process Proves Highly Effective in Level 1 Dual-Lateral Completion, SPE 78697, published 2002 Society of Petroleum Engineers by B. W. McDaniel, et al;
Aliphatic Polyesters: Synthesis, Properties and Applications published 2002, Advances in Polymer Science, Volume 157, Springer-Verlag by Ann-Christine Albertsson, et al;
Controlled Ring-Opening Polymerization of Lactide and Glycolide published 2004 American Chemical Society, Chemical Reviews, A-Z, AA-AD, by Odile Dechy-Cabaret, et al;
Synthetic Polymer Fracturing Fluid for High-Temperature Applications, SPE 80236, published 2003 Society of Petroleum Engineers by Gary P. Funkhouser, et al;
Chelating Agents, Encyclopedia of Chemical Technology, Volume 5, 764-795;

A New Assay for the Enzymatic Degradation of Polylactic Acid, Short Report, published ScienceAsia 29 (2003): 297-300 by Virun Vichaibun, et al;
Patent Application Number 10/864,061 filed 06/09/04, *Aqueous Tackifier and Methods of Controlling Particulates* by Matt Blauch, et al;
Patent Application Number 10/864,618 filed 06/09/04, *Aqueous-Based Tackifier Fluids and Methods of Use* by Matt Blauch, et al.

BROCHURES

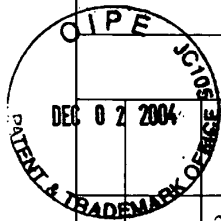
SurgiFracSM Service, A Quick and Cost-Effective Method to Help Boost Production From Openhole Horizontal Completions, HO3297, published 2002 Halliburton Communications;
Cobra FracSM Service, Coiled Tubing Fracturing—Cost-Effective Method for Stimulating Untapped Reserves HO2319R, published 2000 Halliburton Energy Services, Inc;
CobraJet FracSM Service, Cost-effective Technology That Can Help Reduce Cost Per BOE Produced, Shorten Cycle Time and Reduce Capex published Halliburton Communications.

Copies of the aforementioned non-patent references and Form PTO-1449 are submitted herewith.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Robert A. Kent", written over a large, loopy circular flourish.

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580-251-3125



PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al		
Information Disclosure Citation in an Application		Docket Number 2002-IP-009210U1		Group Art Unit	Filing Date 06/27/2003	
U.S. PATENT DOCUMENTS						
	DOCUMENT NO.	ISSUE/ PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
	2,703,316	03-01-55	Palmer	260	78.3	06-05-51
	3,272,650	09-13-66	MacVittie	134	7	02-21-63
	3,819,525	06-25-74	Hattenbrun	252	132	08-21-72
	3,912,692	10-14-75	Casey <i>et al.</i>	260	78.3	09-24-74
	4,172,066	10-23-79	Zweigle <i>et al.</i>	260	29.6TA	09-26-77
	4,460,052	07-17-84	Gockel	175	72	08-10-81
	4,498,995	02-12-85	Gockel	252	8.5LC	07-01-83
	4,797,262	01-10-89	Dewitz	422	142	06-03-87
	5,249,628	10-05-93	Surjaatmadja	166	305	09-29-92
	5,295,542	03-22-94	Cole, <i>et al.</i>	166	278	10-05-92
	5,325,923	07-05-94	Surjaatmadja, <i>et al.</i>	166	308	09-30-93
	5,330,005	07-19-94	Card, <i>et al.</i>	166	280	04-05-93
	5,360,068	11-01-94	Sprunt, <i>et al.</i>	166	259	04-19-93
	5,363,916	11-15-94	Himes, <i>et al.</i>	166	276	06-16-93
	5,373,901	12-20-94	Norman, <i>et al.</i>	166	300	07-27-93
	5,386,874	02-07-95	Laramay, <i>et al.</i>	166	300	11-08-93
	5,396,957	03-14-94	Surjaatmadja, <i>et al.</i>	166	308	03-04-94
	5,402,846	04-04-95	Jennings, Jr., <i>et al.</i>	166	259	11-15-93
	5,464,060	11-07-95	Hale, <i>et al.</i>	166	293	04-12-94
	5,497,830	03-12-96	Boles, <i>et al.</i>	166	300	04-06-95
	5,499,678	03-19-96	Surjaatmadja, <i>et al.</i>	166	298	08-02-94
	5,505,787	04-09-96	Yamaguchi	134	4	01-28-94
	5,512,071	04-30-96	Yam, <i>et al.</i>	51	307	02-25-94
	5,604,186	02-18-97	Hunt, <i>et al.</i>	507	204	02-15-95
	5,670,473	09-23-97	Scepanski	510	445	06-06-95
EXAMINER				DATE CONSIDERED		
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.						

PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al			
Information Disclosure Citation in an Application		Docket Number 2002-IP-009210U1		Group Art Unit		Filing Date 06/27/2003	
U.S. PATENT DOCUMENTS							
		DOCUMENT NO.	ISSUE/ PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
		5,698,322	12-16-97	Tsai, <i>et al.</i>	428	373	12-02-96
		5,765,642	06-16-98	Surjaatmadja	166	297	12-23-96
		5,833,000	11-10-98	Weaver, <i>et al.</i>	166	276	02-18-97
		5,853,048	12-29-98	Weaver, <i>et al.</i>	166	279	04-21-98
		5,893,416	04-13-99	Read	166	304	11-28-97
		5,964,291	10-12-99	Bourne, <i>et al.</i>	166	279	02-28-96
		6,004,400	12-21-99	Bishop, <i>et al.</i>	134	2	07-09-97
		6,024,170	02-15-00	McCabe, <i>et al.</i>	166	300	06-03-98
		6,028,113	02-22-00	Scepanski	514	643	09-27-95
		6,123,965	09-26-00	Jacob, <i>et al.</i>	424	489	08-18-98
		6,135,987	10-24-00	Tsai, <i>et al.</i>	604	365	12-22-99
		6,169,058 B1	01-02-01	Le, <i>et al.</i>	507	222	06-05-97
		6,202,751 B1	03-20-01	Chatterji, <i>et al.</i>	166	276	07-28-00
		6,209,646 B1	04-03-01	Reddy, <i>et al.</i>	166	300	04-21-99
		6,214,773 B1	04-10-01	Harris, <i>et al.</i>	507	271	09-29-99
		6,260,622 B1	07-17-01	Blok, <i>et al.</i>	166	305.1	12-23-98
		6,311,773 B1	11-06-01	Todd, <i>et al.</i>	166	280	01-28-00
		6,357,527 B1	03-19-02	Norman, <i>et al.</i>	166	300	05-05-00
		6,364,945 B1	04-02-02	Chatterji, <i>et al.</i>	106	677	12-13-00
		6,390,195 B1	05-21-02	Nguyen, <i>et al.</i>	166	276	10-27-00
		6,422,314 B1	07-23-02	Todd, <i>et al.</i>	166	312	08-01-00
		6,454,003 B1	09-24-02	Chang, <i>et al.</i>	166	270	06-14-00
		6,488,763 B2	12-03-02	Brothers, <i>et al.</i>	106	692	10-05-01
		6,494,263 B2	12-17-02	Todd	166	312	01-09-01
		6,508,305 B1	01-21-03	Brannon, <i>et al.</i>	166	293	09-14-00
		6,527,051 B1	03-04-03	Reddy, <i>et al.</i>	166	300	07-12-02
		6,554,071 B1	04-29-03	Reddy, <i>et al.</i>	166	293	07-12-02
EXAMINER					DATE CONSIDERED		
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PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al			
Information Disclosure Citation in an Application		Docket Number 2002-IP-009210U1		Group Art Unit		Filing Date 06/27/2003	
U.S. PATENT DOCUMENTS							
		DOCUMENT NO.	ISSUE/PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
		6,569,814 B1	05-27-03	Brady, <i>et al.</i>	507	201	04-20-00
		6,667,279 B1	12-23-03	Hessert, <i>et al.</i>	507	225	11-13-97
		6,681,856 B1	01-27-04	Chatterji, <i>et al.</i>	166	294	05-16-03
		6,686,328 B1	02-03-04	Binder	510	446	07-09-99
		US 2003/0188766A1	10-09-03	Banerjee, <i>et al.</i>	134	7	12-19-02
		US 2004/0055747A1	03-25-04	Lee	166	278	09-20-02
		US 2004/0106525A1	06-03-04	Willbert, <i>et al.</i>	507	200	10-17-03
		US 2004/0138068A1	07-15-04	Rimmer, <i>et al.</i>	507	100	12-19-03
		US 2004/0152601A1	08-05-04	Still, <i>et al.</i>	507	100	10-27-03
		US 2004/0152602A1	08-05-04	Boles	507	100	01-15-04
FOREIGN PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION
							Yes No
		WO 99/27229	06-03-99	PCT	E21B	43/26	X
		WO 01/87797 A1	11-22-01	PCT	C04B	28/02	X
		WO 03/027431 A2	04-03-03	PCT	E21B	-	X
		WO 03/027431 A3	04-03-03	PCT	E21B	43/26	X
		EP 0 510 762 A2	04-16-92	Europe	C11D	17/00	X
EXAMINER					DATE CONSIDERED		
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PTO-1449			Application No. 10/608,291		Applicant(s) Philip D. Nguyen, et al		
Information Disclosure Citation in an Application			Docket Number 2002-IP-009210U1		Group Art Unit	Filing Date 06/27/2003	
FOREIGN PATENT DOCUMENTS							
		DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION Yes No
NON-PATENT DOCUMENTS							
		DOCUMENT (Including Author, Title, Source, and Pertinent Pages)					
		Cantu, et al, <i>Laboratory and Field Evaluation of a Combined Fluid-Loss-Control Additive and Gel Breaker for Fracturing Fluids</i> , SPE 18211, Society of Petroleum Engineers, 1990					
		Love, et al, <i>Selectively Placing Many Fractures in Openhole Horizontal Wells Improves Production</i> , SPE 50422, Society of Petroleum Engineers, 1998					
		McDaniel, et al, <i>Evolving New Stimulation Process Proves Highly Effective in Level 1 Dual-Lateral Completion</i> , SPE 78697, Society of Petroleum Engineers, 2002					
		Albertsson, et al, <i>Aliphatic Polyesters: Synthesis, Properties and Applications</i> , Advances in Polymer Science, Vol. 157, 2002					
		Dechy-Cabaret, et al, <i>Controlled Ring-Opening Polymerization of Lactide and Glycolide</i> , American Chemical Society, Chemical Reviews, A-Z, AA-AD, received 2004					
		Funkhouser, et al, <i>Synthetic Polymer Fracturing Fluid for High-Temperature Applications</i> , SPE 80236, Society of Petroleum Engineers, 2003					
		<i>Chelating Agents</i> , Encyclopedia of Chemical Technology, Vol. 5 (764-795)					
		Vichaibun, et al, <i>A New Assay for the Enzymatic Degradation of Polylactic Acid</i> , Short Report, ScienceAsia, Vol. 29, 2003 (pp. 297-300)					
		Halliburton, <i>SurgiFracSM Service, A Quick and Cost-Effective Method to Help Boost Production From Openhole Horizontal Completions</i> , Halliburton Communications, HO3297, 2002					
		Halliburton, <i>Cobra FracSM Service, Coiled Tubing Fracturing—Cost-Effective Method for Stimulating Untapped Reserves</i> , HO2319R, Halliburton Energy Services, 2000					
		Halliburton, <i>CobraJet FracSM Service, Cost-effective Technology That Can Help Reduce Cost Per BOE Produced, Shorten Cycle Time and Reduce Capex</i> , Halliburton Communications					
		Blauch, et al, <i>Aqueous Tackifier and Methods of Controlling Particulates</i> , Patent Application No. 10/864,061, filed 06-09-04					
		Blauch, et al, <i>Aqueous-Based Tackifier Fluids and Methods of Use</i> , Patent Application No. 10/864,618, filed 06-09-04					
EXAMINER					DATE CONSIDERED		
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.							

IPW



Practitioner's Docket No. 2002-IP-009210U1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of _____
Inventor(s)

for _____
Title of invention

OR

In re application of: Nguyen, et al

Application No.: 10 /608,291

Group Art Unit:

Filed: 06/27/2003

Examiner:

For: Compositions and Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean Well

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT
WITHIN THREE MONTHS OF FILING OR
BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))**

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10*
(When using Express Mail, the Express Mail label number is mandatory;
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

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37 C.F.R. § 1.10 *

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Date: 6-25-04

Signature

Tammy Knight

(type or print name of person certifying)

* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 1 of 3)

NOTE: 37 C.F.R. 1.98(b):

- (1) Each U.S. patent listed in an information disclosure statement must be identified by inventor, patent number, and issue date.
- (2) Each U.S. patent application publication listed in an information disclosure statement shall be identified by applicant, patent application publication number, and publication date.
- (3) Each U.S. application listed in an information disclosure statement must be identified by the inventor, application number, and filing date.
- (4) Each foreign patent or published foreign patent application listed in an information disclosure statement must be identified by the country or patent office which issued the patent or published the application, an appropriate document number, and the publication date indicated on the patent or published application.
- (5) Each publication listed in an information disclosure statement must be identified by publisher, author (if any), title, relevant pages of the publication, date, and place of publication.

WARNING: No extension of time can be had under 37 C.F.R. § 1.136 (a) or (b) for filing an IDS. 37 C.F.R. § 1.97(f).

NOTE: The "filing date of a national application" under 37 C.F.R. § 1.97(b) has two possible meanings. Where the filing is a direct one to the United States Patent & Trademark Office, the filing is defined in 37 C.F.R. § 1.53(b) as "the date on which: (1) A specification containing a description pursuant to § 1.71 and at least one claim pursuant to § 1.75; and (2) any drawing required by § 1.81(a), are filed in the Patent and Trademark Office in the name of the actual inventor or inventors as required by § 1.41." 37 C.F.R. § 1.97(b)(1). On the other hand, an international application that enters the national stage occurs when the applicant has filed the documents and fees required by 35 U.S.C. § 371(c) within the periods set forth in § 1.494 or § 1.495. 35 U.S.C. § 371(c) requires the filing of the following: (1) the basic national fee; (2) a copy of the international application, unless already sent by the International Bureau, and optionally an English translation if filed in another language; and, also optionally (3) amendments under PCT Article 19, with a translation into English if made in another language; (4) an oath or declaration; and (5) a translation into English of any annexes to the international preliminary examination report, if such annexes were made in another language. The optional items must be submitted later, with surcharges. 37 C.F.R. § 1.97(b)(2).

IDENTIFICATION OF TIME OF FILING THE ACCOMPANYING INFORMATION DISCLOSURE STATEMENT

The information disclosure statement submitted herewith is being filed within three months of the filing date of the application or date of entry into the national stage of an international application or before the mailing date of a first Office action on the merits, whichever event occurs last. 37 C.F.R. § 1.97(b).

NOTE: "No certification or fee is due when the filing is made within the above time period. It is advisable to ensure that no Office action has been mailed if the disclosure statement is delayed until after three months from filing."

NOTE: "An information disclosure statement will be considered to have been filed on the day it was received in the Office, or on an earlier date of a mailing if accompanied by a properly executed certificate of mailing under 37 C.F.R. 1.8, or Express Mail certificate under 37 C.F.R. 1.10. An Office action is mailed on the date indicated in the Office action." Notice of April 20, 1992 (1138 O.G. 37-41, 39). See also § 609, M.P.E.P., 8th Edition.

NOTE: "The term 'national application' includes continuing applications (continuations, divisions, continuations-in-part) so three-months will be measured from the actual filing date of an application as opposed [sic] to the effective date of a continuing application." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office
Action [8-3]—page 2 of 3)

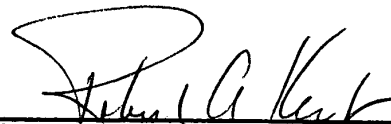
NOTE: "An action on the merits means an action which treats the patentability of the claims in an application, as opposed to only formal or procedural requirements. An action on the merits would, for example, contain a rejection or indication of allowability of a claim or claims rather than just a restriction requirements (37 C.F.R. 1.142) or just a requirement for additional fees to have a claim considered (37 C.F.R. 1.16(d)). Thus, if an application was filed on Jan. 1 and the first Office action on the merits was not mailed until six months later on July 1, the examiner would be required to consider any proper information disclosure statement filed prior to July 1." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

WARNING: "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1992 (1141 O.G. 63). But see § 103(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(d) and in a request for continued examination (RCE) under § 1.114.

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SIGNATURE OF PRACTITIONER

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(type or print name of practitioner)

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Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [8-3]—page 3 of 3)



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Philip D. Nguyen, et al.)	
)	Art Unit: Unknown
)	
Serial No.:	10/608,291)	
)	
Filed:	06/27/2003)	Examiner: Unknown
)	
For:	Compositions and Methods)	
	For Improving Proppant)	
	Pack Permeability and)	
	Fracture Conductivity in)	
	A Subterranean Well)	

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

COMMISSIONER FOR PATENTS
Alexandria, VA 22313-1450

SIR:

The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

U. S. PATENTS

U.S. Patent Number 2,238,671 issued 04/15/41 to John C. Woodhouse;
U.S. Patent Number 3,784,585 issued 01/08/74 to Edward Emil Schmitt, et al;
U.S. Patent Number 3,828,854 issued 08/13/74 to Charles C. Templeton, et al;
U.S. Patent Number 3,868,998 issued 03/04/75 to James H. Lybarger, et al;
U.S. Patent Number 4,169,798 issued 10/02/79 to Ronald N. DeMartino;
U.S. Patent Number 4,470,915 issued 09/11/84 to Michael W. Conway;
U.S. Patent Number 4,716,964 issued 01/05/88 to Steven R. Erbstoesser, et al;

U.S. Patent Number 4,809,783 issued 03/07/89 to Keith H. Hollenbeck, et al;
U.S. Patent Number 4,843,118 issued 06/27/89 to Ta-Wang Lai, et al;
U.S. Patent Number 4,961,466 issued 10/09/90 to Ronald E. Himes, et al;
U.S. Patent Number 4,986,354 issued 01/22/91 to Lisa A. Cantu, et al;
U.S. Patent Number 5,082,056 issued 01/21/92 to James E. Tackett, Jr.;
U.S. Patent Number 5,439,055 issued 08/08/95 to Roger J. Card, et al;
U.S. Patent Number 5,460,226 issued 10/24/95 to Jimmie B. Lawson, et al;
U.S. Patent Number 5,591,700 issued 01/07/97 to Phillip C. Harris, et al;
U.S. Patent Number 6,162,766 issued 12/19/00 to David J. Muir, et al;
U.S. Patent Number 6,189,615 issued 02/20/01 to Robert D. Sydansk;
U.S. Patent Number 6,242,390 issued 06/05/01 to Thomas O. Mitchell, et al;
U.S. Patent Number 6,387,986 issued 05/14/02 to Ahmad Moradi-Araghi, et al;
U.S. Patent Number 6,669,771 issued 12/30/03 to Yutaka Tokiwa, et al;
U.S. Patent Number 6,710,019 issued 03/23/04 to Christopher Alan Sawdon, et al;
U.S. Patent Number 2001/0016562 issued 08/23/01 to David J. Muir, et al;
U.S. Patent Number 2003/0060374 issued 03/27/03 to Claude E. Cooke, Jr.;
U.S. Patent Number 2003/0114314 issued 06/19/03 to David A. Ballard, et al;
U.S. Patent Number 2003/0130133 issued 07/10/03 to Daniel Patrick Vollmer;
U.S. Patent Number 2003/0234103 issued 12/25/03 to Jesse Lee, et al;
U.S. Patent Number 2004/0014607 issued 01/22/04 to A. Richard Sinclair, et al; and
U.S. Patent Number 2004/0040706 issued 03/04/04 to Mohammad Hossaini, et al.

FOREIGN PATENTS

PCT International Publication Number 2004/037946 A1 published 05/06/04 to Dean Willberg, et al; and

PCT International Publication Number 2004/038176 A1 published 05/06/04 to John Still, et al.

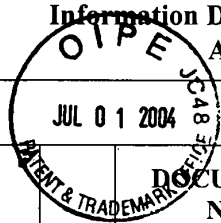
Copies of the aforementioned references and Form PTO-1449 are submitted herewith.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Robert A. Kent". The signature is fluid and cursive, with a large loop at the beginning and a long, sweeping tail.

Robert A. Kent
Registration No. 28,626
Halliburton Energy Services
P. O. Box 1431
Duncan, OK 73536-0440
580-251-3125

PTO-1449		Application No. 10/608,291		Applicant(s) Philip D. Nguyen <i>et al.</i>	
Information Disclosure Citation in an Application		Docket Number 2002-IP-09210U1		Group Art Unit Filing Date 06-27-2003	



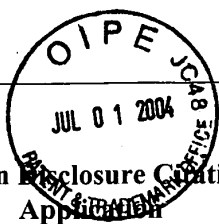
U.S. PATENT DOCUMENTS						
DOCUMENT NO.	ISSUE/ PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE	
2,238,671	04-15-41	Woodhouse	166	21	02-09-40	
3,784,585	01-08-74	Schmitt <i>et al.</i>	260	861	10-21-71	
3,828,854	08-13-74	Templeton <i>et al.</i>	166	307	10-30-73	
3,868,998	03-04-75	Lybarger <i>et al.</i>	166	278	05-15-74	
4,169,798	10-02-79	DeMartino	252	8.55R	10-25-77	
4,470,915	09-11-84	Conway	252	8.55R	09-27-82	
4,716,964	01-05-88	Erbstoesser <i>et al.</i>	166	284	12-10-86	
4,809,783	03-07-89	Hollenbeck <i>et al.</i>	166	307	01-14-88	
4,843,118	06-27-89	Lai <i>et al.</i>	524	555	06-19-87	
4,961,466	10-09-90	Himes <i>et al.</i>	166	250	01-23-89	
4,986,354	01-22-91	Cantu <i>et al.</i>	166	279	09-14-88	
5,082,056	01-21-92	Tackett Jr.	166	295	10-16-90	
5,439,055	08-08-95	Card <i>et al.</i>	166	280	03-08-94	
5,460,226	10-24-95	Lawson <i>et al.</i>	166	300	05-18-94	
5,591,700	01-07-97	Harris <i>et al.</i>	507	204	12-22-94	
6,162,766	12-19-00	Muir <i>et al.</i>	507	267	05-29-98	
6,189,615	02-20-01	Sydansk	166	270	12-15-98	
6,242,390	06-05-01	Mitchell <i>et al.</i>	507	211	07-31-98	
6,387,986	05-04-02	Moradi-Araghi <i>et al.</i>	523	211	06-24-99	

FOREIGN PATENT DOCUMENTS						
DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
					Yes	No
WO 04/038176 A1	05/06/04	United States	E21B	43/27		n/a

NON-PATENT DOCUMENTS	
DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	

EXAMINER	DATE CONSIDERED
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EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.



PTO-1449	Information Disclosure Citation in an Application	Application No. 10/608,291	Applicant(s) Philip D. Nguyen <i>et al.</i>	
		Docket Number 2002-IP-09210U1	Group Art Unit	Filing Date 06-27-2003

U.S. PATENT DOCUMENTS

	DOCUMENT NO.	ISSUE/PUB. DATE	NAME	CLASS	SUBCLASS	FILING DATE
	6,669,771	12-30-03	Tokiwa <i>et al.</i>	106	162	12-08-02
	6,710,019	03-23-04	Sawdon <i>et al.</i>	507	136	07-16-99
	US 2001/0016562	08-23-01	Muir <i>et al.</i>	507	201	11-29-00
	US 2003/0060374	03-27-03	Cooke Jr.	507	200	09-24-02
	US 2003/0114314	06-19-03	Ballard <i>et al.</i>	507	100	12-19-01
	US 2003/0130133	07-10-03	Vallmer	507	100	12-11-02
	US 2003/0234103	12-25-03	Lee <i>et al.</i>	166	293	06-20-02
	US 2004/0014607	01-22-04	Sinclair <i>et al.</i>	507	200	07-16-02
	US 2004/0040706	03-04-04	Hossaini <i>et al.</i>	166	278	08-28-02

FOREIGN PATENT DOCUMENTS

	DOCUMENT NO.	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION	
						Yes	No
	WO 04/037946 A1	05-06-04	United States	C09K	7/00		n/a

NON-PATENT DOCUMENTS

	DOCUMENT (Including Author, Title, Source, and Pertinent Pages)	

EXAMINER	DATE CONSIDERED
EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP § 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to the applicant.	

PATENT APPLICATION FEE DETERMINATION RECORD

Effective January 1, 2003

Application or Docket Number

10608291

CLAIMS AS FILED - PART I

	(Column 1)	(Column 2)
TOTAL CLAIMS	68	
FOR	NUMBER FILED	NUMBER EXTRA
TOTAL CHARGEABLE CLAIMS	68 minus 20 =	48
INDEPENDENT CLAIMS	21 minus 3 =	18
MULTIPLE DEPENDENT CLAIM PRESENT		<input type="checkbox"/>

If the difference in column 1 is less than zero, enter "0" in column 2

CLAIMS AS AMENDED - PART II

	(Column 1)	(Column 2)	(Column 3)
AMENDMENT A	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA
Total	21	Minus 8	
Independent	3	Minus 3	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM			<input type="checkbox"/>

20 36 54

	(Column 1)	(Column 2)	(Column 3)
AMENDMENT B	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA
Total		Minus	
Independent		Minus	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM			<input type="checkbox"/>

	(Column 1)	(Column 2)	(Column 3)
AMENDMENT C	CLAIMS REMAINING AFTER AMENDMENT	HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA
Total		Minus	
Independent		Minus	
FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM			<input type="checkbox"/>

If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
 ** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
 *** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
 The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 2.

SMALL ENTITY TYPE ☐

OTHER THAN SMALL ENTITY OR ☐

RATE	FEE
BASIC FEE	375.00
X\$9=	
X42=	
+140=	
TOTAL	

RATE	FEE
BASIC FEE	750.00
X\$18=	664
X84=	84
+280=	
TOTAL	1698

RATE	ADDITIONAL FEE
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X42=	
+140=	
TOTAL	

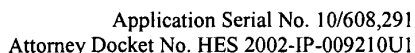
RATE	ADDITIONAL FEE
X\$18=	
X84=	
+280=	
TOTAL	

RATE	ADDITIONAL FEE
X\$9=	
X42=	
+140=	
TOTAL	

RATE	ADDITIONAL FEE
X\$18=	
X84=	
+280=	
TOTAL	

RATE	ADDITIONAL FEE
X\$9=	
X42=	
+140=	
TOTAL	

RATE	ADDITIONAL FEE
X\$18=	
X84=	
+280=	
TOTAL	



In re Application of:

Nguyen, et al

Serial No.: 10/608,291

Filed: **June 27, 2003**

Title: **“COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK PERMEABILITY IN A SUBTERRANEAN WELL”**

~~~~~

Group Art Unit: *Unassigned*

Examiner: *Unassigned*

Atty. Docket No: **HES 2002-IP-009210U1**

**MAIL STOP AMENDMENT**  
**Honorable Commissioner of Patents**  
**P. O. Box 1450**  
**Alexandria, VA 22313-1450**

# CERTIFICATE OF MAILING VIA REGULAR MAIL

ATTY. DOCKET NO.: HES 2002-IP-009210U1  
GROUP ART UNIT: UNASSIGNED  
EXAMINER: UNASSIGNED

PURSUANT TO 37 C.F.R. § 1.10, I HEREBY CERTIFY THAT I HAVE INFORMATION AND A REASONABLE BASIS FOR BELIEF THAT THIS CORRESPONDENCE WILL BE DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS EXPRESS MAIL, POST OFFICE TO ADDRESSEE, ON THE DATE INDICATED BELOW, AND IS ADDRESSED TO:

MAIL STOP AMENDMENT  
HONORABLE COMMISSIONER FOR PATENTS  
P. O. Box 1450  
ALEXANDRIA, VA 22313-1450.

ALEXANDRIA, VA 22313-1450.

Sammy Knight 6-17-04  
TAMMY KNIGHT DATE

## TRANSMITTAL LETTER

Dear Sir:

Applicants hereby submit the following documents to be filed with the United

States Patent and Trademark Office:

1. Preliminary Amendment
2. Return receipt postcard.

Please date stamp and return the enclosed postcard evidencing receipt of these materials.

Applicants believe \$86.00 in fees are due in association with this filing. However, the Commissioner is authorized to debit Deposit Account No. 08-0300 of Halliburton Energy Services, Inc., for any underpayment of fees that may be due.

Respectfully submitted,



Robert A. Kent  
Reg. No. 28,626  
Halliburton Energy Services  
P.O. Box 1431  
Duncan, Oklahoma 73536-0102  
Telephone: (580) 251-3125

**ATTORNEY FOR APPLICANTS**

Date: 6-17-04

Application Serial No. 10/608,291  
Attorney Docket No. HES 2002-IP-009210U1

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

NGUYEN, ET AL

Serial No.: 10/608,291

Filed: **June 27, 2003**

Title: **“COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK PERMEABILITY IN A SUBTERRANEAN WELL”**



Group Art Unit: *Unassigned*

Examiner: *Unassigned*

Atty. Docket No: **HES 2002-IP-009210U1**

**MAIL STOP AMENDMENT**  
**Honorable Commissioner of Patents**  
**P. O. Box 1450**  
**Alexandria, VA 22313-1450**

### CERTIFICATE OF MAILING VIA REGULAR MAIL

ATTY. DOCKET No.: HES 2002-IP-009210U1  
GROUP ART UNIT: UNASSIGNED  
EXAMINER: UNASSIGNED

PURSUANT TO 37 C.F.R. § 1.10, I HEREBY CERTIFY THAT I HAVE INFORMATION AND A REASONABLE BASIS FOR BELIEF THAT THIS CORRESPONDENCE WILL BE DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS EXPRESS MAIL, POST OFFICE TO ADDRESSEE, ON THE DATE INDICATED BELOW, AND IS ADDRESSED TO:

MAIL STOP AMENDMENT  
HONORABLE COMMISSIONER FOR PATENTS  
P. O. Box 1450  
ALEXANDRIA, VA 22313-1450.

ALEXANDRIA, VA 22313-1450.

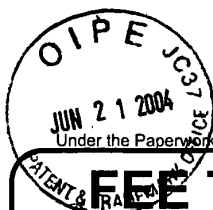
Tammy Knight 6-17-04  
TAMMY KNIGHT DATE

## PRELIMINARY AMENDMENT

Prior to examination on the merits, please amend the application as follows and consider the included remarks. No office action with respect to this case has been issued; therefore, Applicants believe this Preliminary Amendment is timely filed.

06/23/2004 EAREGAY1 00000036 080300 10608291

01 FC:1201 86.00 DA



IFW/K

Approved for use through 07/31/2006. OMB 0651-0032  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

# FEE TRANSMITTAL

## for FY 2004

Effective 10/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT

(\$ 86.00)

### Complete if Known

Application Number 10/608,291  
Filing Date 06/27/2003  
First Named Inventor Nguyen, et al  
Examiner Name  
Art Unit  
Attorney Docket No. 2002-IP-009210U1

### METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☒ Deposit Account:

Deposit Account Number 08-0300  
Deposit Account Name

The Director is authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☒ Credit any overpayments

☐ Charge any additional fee(s) or any underpayment of fee(s)

☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.

### FEE CALCULATION

#### 1. BASIC FILING FEE

| Large Entity |          | Small Entity |          | Fee Description        | Fee Paid |
|--------------|----------|--------------|----------|------------------------|----------|
| Fee Code     | Fee (\$) | Fee Code     | Fee (\$) |                        |          |
| 1001         | 770      | 2001         | 385      | Utility filing fee     |          |
| 1002         | 340      | 2002         | 170      | Design filing fee      |          |
| 1003         | 530      | 2003         | 265      | Plant filing fee       |          |
| 1004         | 770      | 2004         | 385      | Reissue filing fee     |          |
| 1005         | 160      | 2005         | 80       | Provisional filing fee |          |
| SUBTOTAL (1) |          |              |          |                        | (\$)     |

#### 2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

|                    |                      | Extra Claims |                      | Fee from below |                      | Fee Paid             |
|--------------------|----------------------|--------------|----------------------|----------------|----------------------|----------------------|
| Total Claims       | <input type="text"/> | -20** =      | <input type="text"/> | X              | <input type="text"/> | <input type="text"/> |
| Independent Claims | <input type="text"/> | -3** =       | <input type="text"/> | X              | <input type="text"/> | <input type="text"/> |
| Multiple Dependent | <input type="text"/> |              |                      |                | <input type="text"/> | <input type="text"/> |

| Large Entity |          | Small Entity |          | Fee Description                                            | Fee Paid |
|--------------|----------|--------------|----------|------------------------------------------------------------|----------|
| Fee Code     | Fee (\$) | Fee Code     | Fee (\$) |                                                            |          |
| 1202         | 18       | 2202         | 9        | Claims in excess of 20                                     |          |
| 1201         | 86       | 2201         | 43       | Independent claims in excess of 3                          |          |
| 1203         | 290      | 2203         | 145      | Multiple dependent claim, if not paid                      |          |
| 1204         | 86       | 2204         | 43       | ** Reissue independent claims over original patent         |          |
| 1205         | 18       | 2205         | 9        | ** Reissue claims in excess of 20 and over original patent |          |
| SUBTOTAL (2) |          |              |          |                                                            | (\$)     |

\*\*or number previously paid, if greater; For Reissues, see above

### FEE CALCULATION (continued)

#### 3. ADDITIONAL FEES

Large Entity Small Entity

| Fee Code                                         | Fee (\$) | Fee Code | Fee (\$) | Fee Description                                                            | Fee Paid   |
|--------------------------------------------------|----------|----------|----------|----------------------------------------------------------------------------|------------|
| 1051                                             | 130      | 2051     | 65       | Surcharge - late filing fee or oath                                        |            |
| 1052                                             | 50       | 2052     | 25       | Surcharge - late provisional filing fee or cover sheet                     |            |
| 1053                                             | 130      | 1053     | 130      | Non-English specification                                                  |            |
| 1812                                             | 2,520    | 1812     | 2,520    | For filing a request for <i>ex parte</i> reexamination                     |            |
| 1804                                             | 920*     | 1804     | 920*     | Requesting publication of SIR prior to Examiner action                     |            |
| 1805                                             | 1,840*   | 1805     | 1,840*   | Requesting publication of SIR after Examiner action                        |            |
| 1251                                             | 110      | 2251     | 55       | Extension for reply within first month                                     |            |
| 1252                                             | 420      | 2252     | 210      | Extension for reply within second month                                    |            |
| 1253                                             | 950      | 2253     | 475      | Extension for reply within third month                                     |            |
| 1254                                             | 1,480    | 2254     | 740      | Extension for reply within fourth month                                    |            |
| 1255                                             | 2,010    | 2255     | 1,005    | Extension for reply within fifth month                                     |            |
| 1401                                             | 330      | 2401     | 165      | Notice of Appeal                                                           |            |
| 1402                                             | 330      | 2402     | 165      | Filing a brief in support of an appeal                                     |            |
| 1403                                             | 290      | 2403     | 145      | Request for oral hearing                                                   |            |
| 1451                                             | 1,510    | 1451     | 1,510    | Petition to institute a public use proceeding                              |            |
| 1452                                             | 110      | 2452     | 55       | Petition to revive - unavoidable                                           |            |
| 1453                                             | 1,330    | 2453     | 665      | Petition to revive - unintentional                                         |            |
| 1501                                             | 1,330    | 2501     | 665      | Utility issue fee (or reissue)                                             |            |
| 1502                                             | 480      | 2502     | 240      | Design issue fee                                                           |            |
| 1503                                             | 640      | 2503     | 320      | Plant issue fee                                                            |            |
| 1460                                             | 130      | 1460     | 130      | Petitions to the Commissioner                                              |            |
| 1807                                             | 50       | 1807     | 50       | Processing fee under 37 CFR 1.17(q)                                        |            |
| 1806                                             | 180      | 1806     | 180      | Submission of Information Disclosure Stmt                                  |            |
| 8021                                             | 40       | 8021     | 40       | Recording each patent assignment per property (times number of properties) |            |
| 1809                                             | 770      | 2809     | 385      | Filing a submission after final rejection (37 CFR 1.129(a))                |            |
| 1810                                             | 770      | 2810     | 385      | For each additional invention to be examined (37 CFR 1.129(b))             |            |
| 1801                                             | 770      | 2801     | 385      | Request for Continued Examination (RCE)                                    |            |
| 1802                                             | 900      | 1802     | 900      | Request for expedited examination of a design application                  |            |
| Other fee (specify) Additional Independent Claim |          |          |          |                                                                            |            |
| *Reduced by Basic Filing Fee Paid                |          |          |          |                                                                            |            |
| SUBTOTAL (3)                                     |          |          |          |                                                                            | (\$ 86.00) |

### SUBMITTED BY

Name (Print/Type) Robert A. Kent

Registration No. 28,626

(Complete if applicable)

Telephone 580-251-3125

Signature

*Robert A. Kent*

(Attorney/Agent)

Date

6-17-04

**WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

This collection of information is required by 37 CFR 1.17 and 1.27. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.



**CLAIM AMENDMENTS**

Please amend the claims as follows.

1. **(Original)** A method of increasing the conductivity of a fracture in a subterranean formation comprising the steps of:

providing a fracturing treatment fluid comprising a proppant composition, the proppant composition comprising proppant particulates and a degradable material capable of undergoing an irreversible degradation downhole;

introducing the proppant composition to the fracture; and

allowing the proppant composition to form a proppant matrix having voids in the fracture.

2. **(Currently Amended)** The method of claim 1 wherein the proppant particulates comprise sand, walnut hulls, or man-made proppant particulates ~~a man-made proppants~~.

3. **(Currently Amended)** The method of claim 1 wherein the proppant particulates have a size of about 10 to about 60 US mesh.

4. **(Original)** The method of claim 1 wherein the proppant composition further comprises a curable resin, a tackifying agent, or both.

5. **(Original)** The method of claim 4 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.

6. **(Currently Amended)** The method of claim 1 wherein the proppant composition comprises interlocking proppant particulates.

7. **(Original)** The method of claim 1 wherein the degradable material comprises a degradable polymer or a dehydrated salt.

8. **(Currently Amended)** The method of claim 7 wherein the degradable polymer comprises a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly( $\epsilon$ -caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amino acid); a poly(ethylene oxide), or a polyphosphazene ~~polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrate)s, polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.~~

9. **(Original)** The method of claim 1 wherein the degradable material further comprises a plasticizer.

10. **(Original)** The method of claim 7 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

11. **(Original)** The method of claim 1 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

12. **(Original)** The method of claim 1 wherein the degradable material comprises a stereoisomer of a poly(lactide).

13. **(Currently Amended)** The method of claim 1 wherein the proppant composition comprises a poly(lactic acid) degradable material and bauxite proppant particulates, the bauxite proppant particulates at least partially ~~having been~~ coated with a curable epoxy resin, ~~and a polylactic acid degradable material.~~

14. **(Original)** The method of claim 1 wherein the degradable material is present in the proppant composition in an amount sufficient to create a desirable number of voids in the proppant matrix.

15. **(Original)** The method of claim 1 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the composition.
16. **(Original)** The method of claim 1 wherein the degradable material comprises particles having a rod-like shape.
17. **(Original)** The method of claim 1 wherein the degradable material comprises an inorganic or organic compound.
18. **(Original)** The method of claim 17 wherein the inorganic or organic compound comprises sodium acetate trihydrate, L-tartaric acid disodium, salt dihydrate, sodium citrate dihydrate, hydrate of an inorganic acid, hydrate of an inorganic acid salt, sodium tetraborate decahydrate, sodium hydrogenphosphate heptahydrate, sodium phosphate, dodecahydrate, amylose, starch-based hydrophilic polymer, or a cellulose-based hydrophilic polymer.
19. **(Original)** The method of claim 1 wherein the degradable material is a composite.
20. **(Currently Amended)** A method of enhancing the permeability of a proppant matrix comprising the step of introducing **a plurality of** voids into the proppant matrix by a degradation of a degradable material within the **proppant** matrix.
21. **(Currently Amended)** The method of claim 20 wherein the proppant matrix comprises sand, walnut hulls, or **man-made proppant particulates** ~~a man-made proppant particulates~~.
22. **(Original)** The method of claim 20 wherein the proppant matrix comprises a curable resin, a tackifying agent, or both.
23. **(Original)** The method of claim 22 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.

24. **(Original)** The method of claim 20 wherein the proppant matrix comprises interlocking proppant particulates.
25. **(Original)** The method of claim 20 wherein the degradable material comprises a degradable polymer or a dehydrated salt.
26. **(Currently Amended)** The method of claim 25 wherein the degradable polymer comprises a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly( $\epsilon$ -caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amino acid); a poly(ethylene oxide), or a polyphosphazene ~~polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.~~
27. **(Original)** The method of claim 20 wherein the degradable material further comprises a plasticizer.
28. **(Original)** The method of claim 25 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.
29. **(Original)** The method of claim 20 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.
30. **(Original)** The method of claim 20 wherein the degradable material comprises a stereoisomer of a poly(lactide).

31. **(Currently Amended)** The method of claim 20 wherein the proppant matrix comprises a poly(lactic acid) degradable material and bauxite proppant particulates, the bauxite proppant particulates ~~having been~~ at least partially coated with a curable epoxy resin, ~~and a polylactic acid degradable material.~~

32. **(Original)** The method of claim 20 wherein the degradable material is present in the proppant matrix in an amount sufficient to create a desirable number of voids in the proppant matrix.

33. **(Original)** The method of claim 20 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the composition.

34. **(Original)** The method of claim 20 wherein the degradable material comprises particles having a rod-like shape.

35. **(Original)** The method of claim 20 wherein the at least a portion of the voids in the proppant matrix are channel-like in shape.

36. **(Original)** The method of claim 20 wherein the proppant matrix has a conductivity equal to or greater than 4500 darcies at a pressure of about 2000 psi.

37. **(Original)** The method of claim 20 wherein the proppant matrix has a conductivity equal to or greater than 4500 darcies at a pressure of about 4000 psi.

38. **(Original)** The method of claim 20 wherein the proppant matrix has a conductivity equal to or greater than 4000 darcies at a pressure of about 6000 psi.

39. **(Currently Amended)** A proppant matrix composition comprising:  
proppant particulates, the proppant particulates defining a plurality of voids formed by an irreversible degradation of a degradable material and  
a degradable material that undergoes an irreversible degradation downhole.

40. (Currently Amended) The proppant matrix composition of claim 39 wherein the proppant particulates comprise sand, walnut hulls, or man-made proppant particulates ~~a man-made proppant particulates~~.

41. (Currently Amended) The proppant matrix composition of claim 39 wherein the proppant particulates have a size of about 10 to about 60 US mesh.

42. (Currently Amended) The proppant matrix composition of claim 39 wherein the proppant matrix composition further comprises a curable resin, a tackifying agent, or both.

43. (Currently Amended) The proppant matrix composition of claim 42 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.

44. (Currently Amended) The proppant matrix composition of claim 39 wherein the proppant matrix composition comprises interlocking proppant particulates.

45. (Currently Amended) The proppant matrix composition of claim 39 wherein the degradable material comprises a degradable polymer or a dehydrated salt.

46. (Currently Amended) The proppant matrix composition of claim 45 wherein the degradable polymer comprises a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly( $\epsilon$ -caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amino acid); a poly(ethylene oxide), or a polyphosphazene polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrate)s, polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.

47. (Currently Amended) The proppant matrix composition of claim 39 wherein the degradable material further comprises a plasticizer.

48. (Currently Amended) The proppant matrix composition of claim 45 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

49. (Currently Amended) The proppant matrix composition of claim 39 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

50. (Currently Amended) The proppant matrix composition of claim 39 wherein the degradable material comprises a stereoisomer of a poly(lactide).

51. (Currently Amended) The proppant matrix composition of claim 39 wherein the proppant particulates comprise composition comprises a bauxite proppant particulates; ~~the bauxite proppant particulates having been at least partially~~ coated with a curable epoxy resin, and wherein the degradable material comprises poly(lactic acid) a polylactic acid degradable material.

52. (Cancelled)

53. (Currently Amended) The proppant matrix composition of claim 39 wherein the degradable material comprises particles having a rod-like shape.

54. (Currently Amended) The proppant matrix composition of claim 39 wherein the degradable material comprises an inorganic or organic compound.

55. (Currently Amended) The proppant matrix composition of claim ~~54~~ 40 wherein the inorganic or organic compound comprises sodium acetate trihydrate, L-tartaric acid disodium, salt dihydrate, sodium citrate dihydrate, hydrate of an inorganic acid, hydrate of an inorganic acid salt, sodium tetraborate decahydrate, sodium hydrogenphosphate heptahydrate, sodium phosphate, dodecahydrate, amylose, starch-based hydrophilic polymer, or a cellulose-based hydrophilic polymer.

56. **(Currently Amended)** The proppant matrix composition of claim 39 wherein the degradable material is a composite.

57. **(Currently Amended)** A proppant matrix permeability enhancing composition ~~for enhancing the permeability of a proppant matrix~~ comprising proppant particulates and a degradable material.

58. **(Currently Amended)** The composition of claim 57 wherein the proppant particulates comprise sand, walnut hulls, or man-made proppant particulates ~~a man-made proppant particulates~~.

59. **(Currently Amended)** The composition of claim 57 wherein ~~57 wherein~~ the proppant particulates have a size of about 10 to about 60 US mesh.

60. **(Original)** The composition of claim 57 wherein the proppant composition further comprises a curable resin, a tackifying agent, or both.

61. **(Original)** The composition of claim 60 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.

62. **(Original)** The composition of claim 57 wherein the proppant composition comprises interlocking proppant particulates.

63. **(Currently Amended)** The composition of claim 57 wherein ~~57 wherein~~ the degradable material comprises a degradable polymer or a dehydrated salt.



64. **(Currently Amended)** The composition of claim 63 wherein the degradable polymer comprises a polysaccharide, a chitin, a chitosan, a protein, an aliphatic polyester, a poly(lactide), a poly(glycolide), a poly( $\epsilon$ -caprolactone), a poly(hydroxybutyrate), a polyanhydride, an aliphatic polycarbonate, a poly(orthoester), a poly(amino acid); a poly(ethylene oxide), or a polyphosphazene ~~polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrate)s, polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.~~

65. **(Original)** The composition of claim 57 wherein the degradable material further comprises a plasticizer.

66. **(Original)** The composition of claim 63 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

67. **(Original)** The composition of claim 57 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

68. **(Original)** The composition of claim 57 wherein the degradable material comprises a stereoisomer of a poly(lactide).

69. **(Currently Amended)** The composition of claim 57 wherein the proppant composition comprises a poly(lactic acid) degradable material and bauxite proppant particulates, the bauxite proppant particulates having been at least partially coated with a curable epoxy resin, ~~and a polylactic acid degradable material.~~

70. **(Original)** The composition of claim 57 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the proppant composition.

71. **(Original)** The composition of claim 57 wherein the degradable material comprises particles having a rod-like shape.

72. **(New)** A proppant matrix comprising proppant particulates and a plurality of voids, the plurality of voids formed by an irreversible degradation of a degradable material.

**REMARKS**

All amendments are made in a good faith effort to advance the prosecution on the merits of this case. Applicants reserve their rights to subsequently take up prosecution on the claims as originally filed in this or an appropriate continuing application.

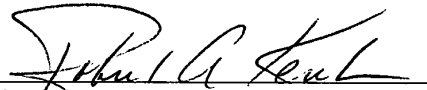
Applicants respectfully request that these amendments above be entered and submit that these amendments will put the claims in condition for allowance. Antecedent basis for these amendments can be found throughout the specification.

**CONCLUSION**

Applicants have made an earnest attempt to place this case in condition for allowance. For the foregoing reasons and for other reasons clearly apparent, Applicants respectfully request full allowance of all pending claims. If the Examiner believes a telephone conference or an interview would advance prosecution of the Application, the undersigned attorney for Applicants is happy to conduct such a conference at the convenience of the Examiner.

Applicants believe \$86.00 in fees are due in association with this filing. However, the Commissioner is authorized to debit Deposit Account No. 08-0300 of Halliburton Energy Services, Inc., for any underpayment of fees that may be due.

Respectfully submitted,



Robert A. Kent  
Reg. No. 28,626  
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Telephone: (580) 251-3125

**ATTORNEY FOR APPLICANTS**

Date: 6-17-04



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Philip D. Nguyen, et al )  
Serial No.: 10/608,291 ) Art Unit: 3672  
Filed: 06/27/2003 ) Examiner: Unknown  
For: Compositions and Methods )  
For Improving Proppant )  
Pack Permeability and )  
Fracture Conductivity )  
In a Subterranean Well )

**SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT**

COMMISSIONER FOR PATENTS  
Alexandria, VA 22313-1450

SIR:


The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

**U. S. PATENTS**

U.S. Patent Number 6,599,863 issued 07/29/03 to Bentley J. Palmer, et al.

Copies of the aforementioned references and Form PTO-1449 are submitted herewith.

Respectfully submitted,

  
Robert A. Kent  
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Halliburton Energy Services  
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Duncan, OK 73536-0440  
580-251-3125



Sheet 1 of 2

|                                                                                                                                                                         |                                      |                          |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|--------------------------|
| <b>FORM PTO-1449 (Modified)</b><br><br>LIST OF PATENTS AND PUBLICATIONS<br>FOR APPLICANT'S INFORMATION<br>DISCLOSURE STATEMENT<br><br>(Use several sheets if necessary) | ATTY. DOCKET NO.<br>2002-IP-009210U1 | SERIAL NO.<br>10/608,291 |
|                                                                                                                                                                         | APPLICANT<br>Philip D. Nguyen, et al |                          |
|                                                                                                                                                                         | FILING DATE<br>06/27/2003            | GROUP<br>3672            |

*U.S. PATENT DOCUMENTS*

| EXAMINER<br>INITIAL |    | Document No. | Date     | Name          | Class | Subclass | Filing<br>Date if<br>Appropriate |
|---------------------|----|--------------|----------|---------------|-------|----------|----------------------------------|
|                     | AA | 6,599,863    | 07/29/03 | Palmer, et al | 507   | 219      |                                  |
|                     | AB |              |          |               |       |          |                                  |
|                     | AC |              |          |               |       |          |                                  |
|                     | AD |              |          |               |       |          |                                  |
|                     | AE |              |          |               |       |          |                                  |
|                     | AF |              |          |               |       |          |                                  |
|                     | AG |              |          |               |       |          |                                  |
|                     | AH |              |          |               |       |          |                                  |
|                     | AI |              |          |               |       |          |                                  |
|                     | AJ |              |          |               |       |          |                                  |
|                     | AK |              |          |               |       |          |                                  |

*FOREIGN PATENT DOCUMENTS*

|  |    | Document No. | Date | Country | Class | Subclass | Translation |    |
|--|----|--------------|------|---------|-------|----------|-------------|----|
|  |    |              |      |         |       |          | Yes         | No |
|  | AL |              |      |         |       |          |             |    |
|  | AM |              |      |         |       |          |             |    |

*OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)*

|  |    |  |  |
|--|----|--|--|
|  | AN |  |  |
|  | AO |  |  |
|  | AP |  |  |

EXAMINER

DATE CONSIDERED

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.



6 m

3672

Applicant's Docket No. 2002-IP-009210U1

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent application

of \_\_\_\_\_  
Inventor(s)

for \_\_\_\_\_  
Title of invention

OR

In re application of: Philip D. Nguyen, et al

Application No.: 10 / 608,291

Group Art Unit: 3672

Filed: 06/27/2003

Examiner:

For: Compositions and Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean Well

Assistant Commissioner for Patents

Washington, D.C. 20231

TRANSMITTAL OF INFORMATION DISCLOSURE STATEMENT  
WITHIN THREE MONTHS OF FILING OR  
BEFORE MAILING OF FIRST OFFICE ACTION (37 C.F.R. § 1.97(b))

CERTIFICATION UNDER 37 C.F.R. §§ 1.8(a) and 1.10\*

(When using Express Mail, the Express Mail label number is mandatory;  
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I hereby certify that, on the date shown below, this correspondence is being:

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37 C.F.R. § 1.8(a)

37 C.F.R. § 1.10\*

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Date: 4-23-04

Signature

Tammy Knight

(type or print name of person certifying)

\* Only the date of filing (§ 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under § 1.8 continues to be taken into account in determining timeliness. See § 1.703(f). Consider "Express Mail Post Office to Addressee" (§ 1.10) or facsimile transmission (§ 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations.

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [6-3]—page 1 of 3)

NOTE: 37 C.F.R. 1.98(b):

- (1) Each U.S. patent listed in an information disclosure statement must be identified by inventor, patent number, and issue date.
- (2) Each U.S. patent application publication listed in an information disclosure statement shall be identified by applicant, patent application publication number, and publication date.
- (3) Each U.S. application listed in an information disclosure statement must be identified by the inventor, application number, and filing date.
- (4) Each foreign patent or published foreign patent application listed in an information disclosure statement must be identified by the country or patent office which issued the patent or published the application, an appropriate document number, and the publication date indicated on the patent or published application.
- (5) Each publication listed in an information disclosure statement must be identified by publisher, author (if any), title, relevant pages of the publication, date, and place of publication.

**WARNING:** No extension of time can be had under 37 C.F.R. § 1.136 (a) or (b) for filing an IDS. 37 C.F.R. § 1.97(f).

**NOTE:** The "filing date of a national application" under 37 C.F.R. § 1.97(b) has two possible meanings. Where the filing is a direct one to the United States Patent & Trademark Office, the filing is defined in 37 C.F.R. § 1.53(b) as "the date on which: (1) A specification containing a description pursuant to § 1.71 and at least one claim pursuant to § 1.75; and (2) any drawing required by § 1.81(a), are filed in the Patent and Trademark Office in the name of the actual inventor or inventors as required by § 1.41." 37 C.F.R. § 1.97(b)(1). On the other hand, an international application that enters the national stage occurs when the applicant has filed the documents and fees required by 35 U.S.C. § 371(c) within the periods set forth in § 1.494 or § 1.495. 35 U.S.C. § 371(c) requires the filing of the following: (1) the basic national fee; (2) a copy of the international application, unless already sent by the International Bureau, and optionally an English translation if filed in another language; and, also optionally (3) amendments under PCT Article 19, with a translation into English if made in another language; (4) an oath or declaration; and (5) a translation into English of any annexes to the international preliminary examination report, if such annexes were made in another language. The optional items must be submitted later, with surcharges. 37 C.F.R. § 1.97(b)(2).

### **IDENTIFICATION OF TIME OF FILING THE ACCOMPANYING INFORMATION DISCLOSURE STATEMENT**

The information disclosure statement submitted herewith is being filed within three months of the filing date of the application or date of entry into the national stage of an international application or before the mailing date of a first Office action on the merits, whichever event occurs last. 37 C.F.R. § 1.97(b).

**NOTE:** "No certification or fee is due when the filing is made within the above time period. It is advisable to ensure that no Office action has been mailed if the disclosure statement is delayed until after three months from filing."

**NOTE:** "An information disclosure statement will be considered to have been filed on the day it was received in the Office, or on an earlier date of a mailing if accompanied by a properly executed certificate of mailing under 37 C.F.R. 1.8, or Express Mail certificate under 37 C.F.R. 1.10. An Office action is mailed on the date indicated in the Office action." Notice of April 20, 1992 (1138 O.G. 37-41, 39). See also § 609, M.P.E.P., 8th Edition.

**NOTE:** "The term 'national application' includes continuing applications (continuations, divisions, continuations-in-part) so three-months will be measured from the actual filing date of an application as opposed [sic] to the effective date of a continuing application." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office  
Action [6-3]—page 2 of 3)




**NOTE:** "An action on the merits means an action which treats the patentability of the claims in an application, as opposed to only formal or procedural requirements. An action on the merits would, for example, contain a rejection or indication of allowability of a claim or claims rather than just a restriction requirements (37 C.F.R. 1.142) or just a requirement for additional fees to have a claim considered (37 C.F.R. 1.16(d)). Thus, if an application was filed on Jan. 1 and the first Office action on the merits was not mailed until six months later on July 1, the examiner would be required to consider any proper information disclosure statement filed prior to July 1." Notice of April 20, 1992 (1138 O.G. 37-41, 39).

**WARNING:** "A petition for suspension of action to allow applicant time to submit an information disclosure statement will be denied as failing to present good and sufficient reasons, since 37 C.F.R. § 1.97 provides adequate recourse for the timely submission of prior art for consideration by the examiner." Notice of July 6, 1992 (1141 O.G. 63). But see § 103(b) and (c), limited suspension of action in a continued prosecution application (CPA) filed under § 1.53(d) and in a request for continued examination (RCE) under § 1.114.

Reg. No.: 28,626

Tel. No.: (580) 251-3125

Customer No.:



SIGNATURE OF PRACTITIONER

Robert A. Kent

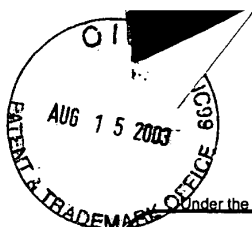
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Duncan, OK 73536-0440

(Transmittal of Information Disclosure Statement Within Three Months of Filing or Before Mailing of First Office Action [6-3]—page 3 of 3)



PTO/SB/21 (03-03)  
Approved for use through 04/30/2003. OMB 0651-0031  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE  
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

|                                                                                         |                        |                  |
|-----------------------------------------------------------------------------------------|------------------------|------------------|
| <b>TRANSMITTAL FORM</b><br><br>(to be used for all correspondence after initial filing) | Application Number     | 10/608,291       |
|                                                                                         | Filing Date            | 06/27/2003       |
|                                                                                         | First Named Inventor   | Philip D. Nguyen |
|                                                                                         | Art Unit               |                  |
|                                                                                         | Examiner Name          |                  |
| Total Number of Pages in This Submission                                                | Attorney Docket Number | 2002-IP-009210U1 |

| ENCLOSURES (Check all that apply)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <input type="checkbox"/> Fee Transmittal Form<br><input type="checkbox"/> Fee Attached<br><input type="checkbox"/> Amendment/Reply<br><input type="checkbox"/> After Final<br><input type="checkbox"/> Affidavits/declaration(s)<br><input type="checkbox"/> Extension of Time Request<br><input type="checkbox"/> Express Abandonment Request<br><input type="checkbox"/> Information Disclosure Statement<br><input type="checkbox"/> Certified Copy of Priority Document(s)<br><input type="checkbox"/> Response to Missing Parts/Incomplete Application<br><input type="checkbox"/> Response to Missing Parts under 37 CFR 1.52 or 1.53 | <input type="checkbox"/> Drawing(s)<br><input type="checkbox"/> Licensing-related Papers<br><input type="checkbox"/> Petition<br><input type="checkbox"/> Petition to Convert to a Provisional Application<br><input type="checkbox"/> Power of Attorney, Revocation<br><input type="checkbox"/> Change of Correspondence Address<br><input type="checkbox"/> Terminal Disclaimer<br><input type="checkbox"/> Request for Refund<br><input type="checkbox"/> CD, Number of CD(s) _____ | <input type="checkbox"/> After Allowance Communication to a Technology Center (TC)<br><input type="checkbox"/> Appeal Communication to Board of Appeals and Interferences<br><input type="checkbox"/> Appeal Communication to TC (Appeal Notice, Brief, Reply Brief)<br><input type="checkbox"/> Proprietary Information<br><input type="checkbox"/> Status Letter<br><input checked="" type="checkbox"/> Other Enclosure(s) (please identify below):<br><i>Supplemental IDS<br/>PTO 1449</i> |
| Remarks<br>Supplemental IDS & PTO-1449                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |

| SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT |                       |
|--------------------------------------------|-----------------------|
| Firm or Individual                         | Robert A. Kent        |
| Signature                                  | <i>Robert A. Kent</i> |
| Date                                       | 8-12-03               |

| CERTIFICATE OF TRANSMISSION/MAILING                                                                                                                                                                                                                                                           |                        |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, Washington, DC 20231 on this date: <u>8-12-03</u> |                        |
| Typed or printed                                                                                                                                                                                                                                                                              | Tammy L. Knight        |
| Signature                                                                                                                                                                                                                                                                                     | <i>Tammy L. Knight</i> |
| Date                                                                                                                                                                                                                                                                                          | 8-12-03                |

This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, Washington, DC 20231.

If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.



PATENT 2002-IP-009210U1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

|             |                          |   |                   |
|-------------|--------------------------|---|-------------------|
| Applicants: | Philip D. Nguyen, et al  | ) |                   |
| Serial No.: | 10/608,291               | ) | Art Unit: Unknown |
| Filed:      | 06/27/2003               | ) |                   |
| For:        | Compositions and Methods | ) | Examiner: Unknown |
|             | For Improving Proppant   | ) |                   |
|             | Pack Permeability and    | ) |                   |
|             | Fracture Conductivity in | ) |                   |
|             | A Subterranean Well      | ) |                   |

**SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT**

COMMISSIONER FOR PATENTS  
Alexandria, VA 22313-1450

SIR:

The following documents are known to Applicants or Applicants' attorneys and are submitted for the Examiner to consider in the above-captioned application.

Each item of information contained in this supplemental information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three (3) months prior to the filing of the information disclosure statement.

**U. S. PATENTS**

U.S. Patent Number 3,955,993 issued 05/11/76 to Beverly A. Curtice, et al;

U.S. Patent Number 3,948,672 issued 04/06/76 to Bobby G. Harnsberger;

U.S. Patent Number 6,485,947 issued 11/26/02 to Vineet Rajgarhia, et al;

U.S. Patent Number 4,526,695 issued 07/02/85 to Steven R. Erbstoesser, et al;

U.S. Patent Number 6,172,011 issued 01/09/01 to Roger J. Card, et al;  
U.S. Patent Number 5,924,488 issued 07/20/99 to Philip D. Nguyen, et al;  
U.S. Patent Number 6,209,643 issued 04/03/01 to Philip D. Nguyen, et al;  
U.S. Patent Number 6,047,772 issued 04/11/00 to Jim D. Weaver, et al;  
U.S. Patent Number 5,908,073 issued 06/01/99 to Philip D. Nguyen, et al;  
U.S. Patent Number 5,791,415 issued 08/11/98 to Philip D. Nguyen, et al;  
U.S. Patent Number 4,694,905 issued 09/22/87 to David R. Armbruster;  
U.S. Patent Number 4,785,884 issued 11/22/88 to David R. Armbruster; and  
U.S. Patent Number 6,328,105 issued 12/11/01 to Donald E. Betzold.

**FOREIGN PATENTS**

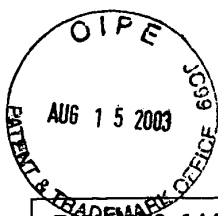
International Publication Number WO 03/02731 issued 04/03/03 by Claude E. Cooke, Jr.

Copies of the aforementioned references and Form PTO-1449 are submitted herewith.

Respectfully submitted,



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Sheet 1 of 1

|                                                                                                                                                                         |                                      |                          |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|--------------------------|
| <b>FORM PTO-1449 (Modified)</b><br><br>LIST OF PATENTS AND PUBLICATIONS<br>FOR APPLICANT'S INFORMATION<br>DISCLOSURE STATEMENT<br><br>(Use several sheets if necessary) | ATTY. DOCKET NO.<br>2002-IP-009210U1 | SERIAL NO.<br>10/608,291 |
|                                                                                                                                                                         | APPLICANT<br>Philip D. Nguyen, et al |                          |
|                                                                                                                                                                         | FILING DATE<br>06/27/03              | GROUP                    |

**U.S. PATENT DOCUMENTS**

| EXAMINER<br>INITIAL |    | Document No. | Date     | Name               | Class | Subclass | Filing<br>Date if<br>Appropriate |
|---------------------|----|--------------|----------|--------------------|-------|----------|----------------------------------|
|                     | AA | 3,955,993    | 05/11/76 | Curtice, et al     | 106   | 662      |                                  |
|                     | AB | 3,948,672    | 04/06/76 | Harnsberger        | 106   | 720      |                                  |
|                     | AC | 6,485,947    | 11/26/02 | Rajgarhia, et al   | 435   | 139      |                                  |
|                     | AD | 4,526,695    | 07/02/85 | Erbstoesser, et al | 507   | 219      |                                  |
|                     | AE | 6,172,011    | 01/09/01 | Card, et al        | 507   | 204      |                                  |
|                     | AF | 5,924,488    | 07/20/99 | Nguyen, et al      | 166   | 280      |                                  |
|                     | AG | 6,209,643    | 04/03/01 | Nguyen, et al      | 166   | 276      |                                  |
|                     | AH | 6,047,772    | 04/11/00 | Weaver, et al      | 166   | 276      |                                  |
|                     | AI | 5,908,073    | 06/01/99 | Nguyen, et al      | 166   | 276      |                                  |
|                     | AJ | 5,791,415    | 08/11/98 | Nguyen, et al      | 166   | 280      |                                  |
|                     | AK | 4,694,905    | 09/22/87 | Armbruster         | 166   | 280      |                                  |
|                     | AL | 4,785,884    | 11/22/88 | Armbruster         | 166   | 280      |                                  |
|                     | AM | 6,328,105    | 12/11/01 | Betzold            | 166   | 280      |                                  |

**FOREIGN PATENT DOCUMENTS**

|  |    | Document No. | Date     | Country       | Class | Subclass | Translation |    |
|--|----|--------------|----------|---------------|-------|----------|-------------|----|
|  |    |              |          |               |       |          | Yes         | No |
|  | AN | WO 03/027431 | 04/03/03 | United States | E2    | 1B       | X           |    |
|  | AO |              |          |               |       |          |             |    |
|  | AP |              |          |               |       |          |             |    |
|  | AQ |              |          |               |       |          |             |    |
|  | AR |              |          |               |       |          |             |    |

**OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)**

|  |    |  |
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|  | AS |  |
|  | AT |  |
|  | AU |  |

EXAMINER

DATE CONSIDERED

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

|                                                                                                                              |                               |                                        |
|------------------------------------------------------------------------------------------------------------------------------|-------------------------------|----------------------------------------|
| <b>UTILITY<br/>PATENT APPLICATION<br/>TRANSMITTAL</b><br><br>(Only for new nonprovisional applications under 37 CFR 1.53(b)) | <b>Attorney Docket No.</b>    | 2002-IP-009210U1                       |
|                                                                                                                              | <b>First Inventor</b>         | Philip D. Nguyen, et al                |
|                                                                                                                              | <b>Title</b>                  | Compositions and Methods for Improving |
|                                                                                                                              | <b>Express Mail Label No.</b> | EU265557354US                          |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                            |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>APPLICATION ELEMENTS</b><br><i>See MPEP chapter 600 concerning utility patent application contents.</i>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | <b>ADDRESS TO:</b> Assistant Commissioner for Patents<br>Box Patent Application<br>Washington, DC 20231                                                                                    |
| 1. <input checked="" type="checkbox"/> Fee Transmittal Form (e.g., PTO/SB/17)<br>(Submit an original and a duplicate for fee processing)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 7. <input type="checkbox"/> CD-ROM or CD-R in duplicate, large table or<br>Computer Program (Appendix)                                                                                     |
| 2. <input type="checkbox"/> Applicant claims small entity status.<br>See 37 CFR 1.27.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 8. Nucleotide and/or Amino Acid Sequence Submission<br>(if applicable, all necessary)                                                                                                      |
| 3. <input checked="" type="checkbox"/> Specification [Total Pages 21]<br>(preferred arrangement set forth below) <ul style="list-style-type: none"><li>- Descriptive title of the invention</li><li>- Cross Reference to Related Applications</li><li>- Statement Regarding Fed sponsored R &amp; D</li><li>- Reference to sequence listing, a table,<br/>or a computer program listing appendix</li><li>- Background of the Invention</li><li>- Brief Summary of the Invention</li><li>- Brief Description of the Drawings (if filed)</li><li>- Detailed Description</li><li>- Claim(s)</li><li>- Abstract of the Disclosure</li></ul> | a. <input type="checkbox"/> Computer Readable Form (CRF)                                                                                                                                   |
| 4. <input type="checkbox"/> Drawing(s) (35 U.S.C. 113) [Total Sheets ]                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | b. Specification Sequence Listing on: <ul style="list-style-type: none"><li>i. <input type="checkbox"/> CD-ROM or CD-R (2 copies); or</li><li>ii. <input type="checkbox"/> paper</li></ul> |
| 5. Oath or Declaration [Total Pages 3] <ul style="list-style-type: none"><li>a. <input checked="" type="checkbox"/> Newly executed (original or copy)</li><li>b. <input type="checkbox"/> Copy from a prior application (37 CFR 1.63 (d))<br/>(for continuation/divisional with Box 18 completed)<ul style="list-style-type: none"><li>i. <input type="checkbox"/> <b>DELETION OF INVENTOR(S)</b><br/>Signed statement attached deleting inventor(s)<br/>named in the prior application, see 37 CFR<br/>1.63(d)(2) and 1.33(b).</li></ul></li></ul>                                                                                     | c. <input type="checkbox"/> Statements verifying identity of above copies                                                                                                                  |
| 6. <input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | <b>ACCOMPANYING APPLICATION PARTS</b>                                                                                                                                                      |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 9. <input checked="" type="checkbox"/> Assignment Papers (cover sheet & document(s))                                                                                                       |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 10. <input checked="" type="checkbox"/> 37 CFR 3.73(b) Statement [Power of Attorney]<br>(when there is an assignee)                                                                        |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 11. <input type="checkbox"/> English Translation Document (if applicable)                                                                                                                  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 12. <input checked="" type="checkbox"/> Information Disclosure Statement (IDS)/PTO-1449 [Copies of IDS Citations]                                                                          |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 13. <input type="checkbox"/> Preliminary Amendment                                                                                                                                         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 14. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503)<br>(Should be specifically itemized)                                                                            |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 15. <input type="checkbox"/> Certified Copy of Priority Document(s)<br>(if foreign priority is claimed)                                                                                    |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 16. <input type="checkbox"/> Nonpublication Request under 35 U.S.C. 122<br>(b)(2)(B)(i). Applicant must attach form PTO/SB/35<br>or its equivalent.                                        |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 17. <input checked="" type="checkbox"/> Other: Express Mail Certificate                                                                                                                    |

18. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment, or in an Application Data Sheet under 37 CFR 1.76:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No. \_\_\_\_\_

Prior application information:

Examiner: \_\_\_\_\_

Group Art Unit: \_\_\_\_\_

For CONTINUATION OR DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

|                                                            |                             |                                                     |              |                                                                     |              |
|------------------------------------------------------------|-----------------------------|-----------------------------------------------------|--------------|---------------------------------------------------------------------|--------------|
| <b>19. CORRESPONDENCE ADDRESS</b>                          |                             |                                                     |              |                                                                     |              |
| <input type="checkbox"/> Customer Number or Bar Code Label |                             | (Insert Customer No. or Attach bar code label here) |              | or <input checked="" type="checkbox"/> Correspondence address below |              |
| Name                                                       | Robert A. Kent              |                                                     |              |                                                                     |              |
| Address                                                    | Halliburton Energy Services |                                                     |              |                                                                     |              |
|                                                            | 2600 South 2nd Street       |                                                     |              |                                                                     |              |
| City                                                       | Duncan                      | State                                               | OK           | Zip Code                                                            | 73536        |
| Country                                                    | USA                         | Telephone                                           | 580-251-3125 | Fax                                                                 | 580-251-3917 |

|                   |                       |                                   |         |
|-------------------|-----------------------|-----------------------------------|---------|
| Name (Print/Type) | Robert A. Kent        | Registration No. (Attorney/Agent) | 28,626  |
| Signature         | <i>Robert A. Kent</i> | Date                              | 6-25-03 |

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231.

17691 U.S. PTO  
06/27/03

PTO/SB/17 (01-03)  
Approved for use through 04/30/2003. OMB 0651-0032  
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# FEE TRANSMITTAL for FY 2003

Effective 01/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$ 1738.00

## Complete if Known

Application Number  
Filing Date  
First Named Inventor Philip D. Nguyen, et al  
Examiner Name  
Art Unit  
Attorney Docket No. 2002-IP-009210U1

## METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☒ Deposit Account:

Deposit Account Number 08-0300

Deposit Account Name

The Commissioner is authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☒ Credit any overpayments

☐ Charge any additional fee(s) during the pendency of this application

☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.

## FEE CALCULATION

### 1. BASIC FILING FEE

| Large Entity Fee Code (\$) | Small Entity Fee Code (\$) | Fee Description        | Fee Paid   |
|----------------------------|----------------------------|------------------------|------------|
| 1001 750                   | 2001 375                   | Utility filing fee     | 750        |
| 1002 330                   | 2002 165                   | Design filing fee      |            |
| 1003 520                   | 2003 260                   | Plant filing fee       |            |
| 1004 750                   | 2004 375                   | Reissue filing fee     |            |
| 1005 160                   | 2005 80                    | Provisional filing fee |            |
| SUBTOTAL (1)               |                            |                        | (\$ 750.00 |

### 2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

Total Claims 68 -20\*\* = 48 x 18 = 864  
Independent Claims 4 -3\*\* = 1 x 84 = 84  
Multiple Dependent

| Large Entity Fee Code (\$) | Small Entity Fee Code (\$) | Fee Description                                            | Fee Paid   |
|----------------------------|----------------------------|------------------------------------------------------------|------------|
| 1202 18                    | 2202 9                     | Claims in excess of 20                                     |            |
| 1201 84                    | 2201 42                    | Independent claims in excess of 3                          |            |
| 1203 280                   | 2203 140                   | Multiple dependent claim, if not paid                      |            |
| 1204 84                    | 2204 42                    | ** Reissue independent claims over original patent         |            |
| 1205 18                    | 2205 9                     | ** Reissue claims in excess of 20 and over original patent |            |
| SUBTOTAL (2)               |                            |                                                            | (\$ 948.00 |

\*\*or number previously paid, if greater; For Reissues, see above

## FEE CALCULATION (continued)

### 3. ADDITIONAL FEES

| Large Entity Fee Code (\$) | Small Entity Fee Code (\$) | Fee Description                                                            | Fee Paid |
|----------------------------|----------------------------|----------------------------------------------------------------------------|----------|
| 1051 130                   | 2051 65                    | Surcharge - late filing fee or oath                                        |          |
| 1052 50                    | 2052 25                    | Surcharge - late provisional filing fee or cover sheet                     |          |
| 1053 130                   | 1053 130                   | Non-English specification                                                  |          |
| 1812 2,520                 | 1812 2,520                 | For filing a request for <i>ex parte</i> reexamination                     |          |
| 1804 920*                  | 1804 920*                  | Requesting publication of SIR prior to Examiner action                     |          |
| 1805 1,840*                | 1805 1,840*                | Requesting publication of SIR after Examiner action                        |          |
| 1251 110                   | 2251 55                    | Extension for reply within first month                                     |          |
| 1252 410                   | 2252 205                   | Extension for reply within second month                                    |          |
| 1253 930                   | 2253 465                   | Extension for reply within third month                                     |          |
| 1254 1,450                 | 2254 725                   | Extension for reply within fourth month                                    |          |
| 1255 1,970                 | 2255 985                   | Extension for reply within fifth month                                     |          |
| 1401 320                   | 2401 160                   | Notice of Appeal                                                           |          |
| 1402 320                   | 2402 160                   | Filing a brief in support of an appeal                                     |          |
| 1403 280                   | 2403 140                   | Request for oral hearing                                                   |          |
| 1451 1,510                 | 1451 1,510                 | Petition to institute a public use proceeding                              |          |
| 1452 110                   | 2452 55                    | Petition to revive - unavoidable                                           |          |
| 1453 1,300                 | 2453 650                   | Petition to revive - unintentional                                         |          |
| 1501 1,300                 | 2501 650                   | Utility issue fee (or reissue)                                             |          |
| 1502 470                   | 2502 235                   | Design issue fee                                                           |          |
| 1503 630                   | 2503 315                   | Plant issue fee                                                            |          |
| 1460 130                   | 1460 130                   | Petitions to the Commissioner                                              |          |
| 1807 50                    | 1807 50                    | Processing fee under 37 CFR 1.17(q)                                        |          |
| 1806 180                   | 1806 180                   | Submission of Information Disclosure Stmt                                  |          |
| 8021 40                    | 8021 40                    | Recording each patent assignment per property (times number of properties) | 40       |
| 1809 750                   | 2809 375                   | Filing a submission after final rejection (37 CFR 1.129(a))                |          |
| 1810 750                   | 2810 375                   | For each additional invention to be examined (37 CFR 1.129(b))             |          |
| 1801 750                   | 2801 375                   | Request for Continued Examination (RCE)                                    |          |
| 1802 900                   | 1802 900                   | Request for expedited examination of a design application                  |          |

Other fee (specify)

\*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$ 40.00

## SUBMITTED BY

|                   |                       |                                   |         |           |              |
|-------------------|-----------------------|-----------------------------------|---------|-----------|--------------|
| Name (Print/Type) | Robert A. Kent        | Registration No. (Attorney/Agent) | 28,626  | Telephone | 580-251-3125 |
| Signature         | <i>Robert A. Kent</i> | Date                              | 6-25-03 |           |              |

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This collection of information is required by 37 CFR 1.17 and 1.27. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, Washington, DC 20231.

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Practitioner's Dock t No. 2002-IP-009210U1

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: Philip D. Nguyen, et al  
Application No.: 0 / Unknown Group No.: Unknown  
Filed: Concurrently Herewith Examiner: Unknown  
For: Compositions and Methods for Improving Proppant Pack Permeability  
and Fracture Conductivity in a Subterranean Well

Assistant Commissioner for Patents  
Washington, D.C. 20231

**EXPRESS MAIL CERTIFICATE**

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Date of Deposit 6-27-2003

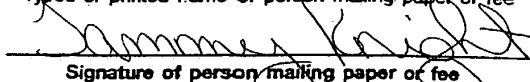
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Specification with 21 Pages Return Postcard  
Information Disclosure Statement with PTO-1449 & References  
Declaration  
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Statement Under 37 CFR 3.73(b)  
Assignment with Recordation Sheet  
Fee Transmittal  
Patent Application Transmittal

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10, on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

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(Express Mail Certificate [B-31])



**COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK  
PERMEABILITY AND FRACTURE CONDUCTIVITY  
IN A SUBTERRANEAN WELL**

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

[001] The present invention relates to enhancing fluid flow from subterranean formations. More particularly, this invention relates to providing improved proppant matrixes within fractures in a subterranean formation.

**2. Description of the Prior Art**

[002] Hydraulic fracturing is a technique for stimulating the production of a subterranean formation. The technique normally involves (1) injecting a viscous liquid through a wellbore into a formation at a chosen rate and pressure to overcome the earth's stresses and form a fracture in the formation; and (2) placing proppant particulates in the fracture to, *inter alia*, maintain the fracture in a propped condition when the injection pressure is released. The resultant propped fracture provides a conductive channel in the formation for fluids to flow to the wellbore.

[003] The degree of stimulation afforded by the hydraulic fracture treatment is largely dependent on the permeability and width of the propped fracture. Thus, the productivity of the well in effect becomes a function of fracture conductivity. To enhance well productivity, it may be necessary to enhance fracture conductivity.

[004] Oftentimes, to effectively prop open the fractures as well as prevent proppant particulate flowback, the proppant particulates are caused to consolidate into proppant matrixes within the fractures. One conventional means of doing this is to use resin-coated proppant particulates so that when the resin cures downhole, the proppant particulates can consolidate into a mass within the fractures. Other methods have also been used to facilitate the consolidation of the proppant particulates within the fractures.

[005] Although consolidating the proppant particulates within a fracture may have some benefits, for example preventing proppant particulate flowback, such methods may adversely affect the conductivity of the fracture. That is, some methods of consolidating proppant particulates themselves may introduce a barrier to the free flow of fluids from the subterranean formation to the wellbore for subsequent production.

Fracture conductivity may suffer as a result. This is undesirable as this may affect overall well productivity.

[006] To counteract this potential problem, many different techniques have been developed. One technique involves adding calcium carbonate or salt to the proppant composition. When the proppant particulates consolidate, after a subsequent fluid is added to the wellbore, the calcium carbonate or salt is dissolved out of the matrix. At least one problem associated with this method is the incomplete removal of the calcium carbonate or salt if not adequately contacted with the subsequent fluid. Another method has been to add wax beads to the proppant composition. Once incorporated into the consolidated proppant particulates, the wax beads melt as a result of the temperature of the formation. A problem with this method is that the wax may re-solidify in the well causing countless problems. Another method that has been used is to add an oil-soluble resin to the proppant composition, however, this method has not been successful because of, *inter alia*, nonuniform removal of the particles.

[007] Another way to address fracture conductivity and proppant matrix permeability has been to use bigger proppant particulates. However, there are practical limits to the size of the proppant that may be used. For instance, if too large of particles are used, premature screen out at the perforations and/or fractures during the proppant stage of fracturing treatment often occurs as large size proppant particulates are being injected into the fractures. In addition, by using too large of proppant particles, the ability to control formation sand is lost as the formation sand or fines tend to invade or penetrate the large pore space of the proppant pack during production of hydrocarbons, thus choking the flow paths of the fluids.

### **SUMMARY OF THE INVENTION**

[008] The present invention relates to enhancing fluid flow from subterranean formations. More particularly, this invention relates to providing improved proppant matrixes within fractures in a subterranean formation.

[009] An example of the methods of the present invention of increasing the conductivity of a fracture in a subterranean formation comprises the steps of providing a fracturing treatment fluid comprising a proppant composition, the proppant composition comprising proppant particulates and a degradable material capable of undergoing an irreversible degradation downhole; introducing the proppant composition to the fracture; and allowing the proppant composition to form a proppant matrix having voids in the fracture.

[010] An example of the proppant compositions of the present invention comprises proppant particulates, and a degradable material that undergoes an irreversible degradation downhole.

[011] The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments which follows.

## DESCRIPTION OF PREFERRED EMBODIMENTS

[012] The present invention provides improved compositions and methods for enhancing fluid flow from a subterranean formation. In preferred embodiments, the present invention provides compositions and methods for enhancing subterranean well productivity by enhancing fracture conductivity. The compositions and methods of the present invention may be used to enhance the permeability of proppant matrixes within fractures so that fluids from the subterranean formation may flow more freely to the wellbore without negatively affecting the ability of the proppant matrix to perform other desired functions within the fracture, *e.g.*, maintaining the integrity of a fracture or providing a sand control means.

[013] The proppant compositions of the present invention may be used in conjunction with any suitable fracturing fluid. These compositions comprise proppant particulates and a degradable material capable of undergoing an irreversible degradation downhole. The term "irreversible" as used herein means that the degradable material once degraded downhole, it should not recrystallize or reconsolidate while downhole, *e.g.*, the degradable material should degrade *in situ* but should not recrystallize or reconsolidate *in situ*. The terms "degradation" or "degradable" refer to both the two relatively extreme cases of hydrolytic degradation that the degradable material may undergo, *i.e.*, heterogeneous (or bulk erosion) and homogeneous (or surface erosion), and any stage of degradation in between these two. This degradation can be a result of, *inter alia*, a chemical or thermal reaction or a reaction induced by radiation.

[014] Any proppant particulate suitable for use in subterranean applications is suitable for use in the compositions and methods of the present invention. For instance, natural sand, ground walnut hulls, man-made proppants, including bauxite, ceramics, polymeric materials, or the like are suitable. Suitable sizes range from 4 to 100 U.S. mesh, but are preferably in the range of 10 to 60 US mesh. In some embodiments, the proppant particulates may be coated with a curable resin. Even though using proppant particulates that have been coated with curable resin is preferable, the methods of the present invention are applicable for use with uncoated proppant particulates.

[015] If a curable resin is used, the proppant particulates can either be precoated or coated on-the-fly with a curable resin. Any type of curable resin that will

enable the proppant particulates to consolidate within a fracture in the formation is suitable for use in the present invention, *e.g.*, epoxies, furan, phenolics, furfuryl aldehyde, furfuryl alcohol, or mixtures thereof. If a curable resin is utilized, preferably the proppant particulates are coated with a curable resin prior to being mixed with the degradable material. Any portion of the proppant particulates may be coated with a curable resin. For instance, just the tail-end portion, the first portion and the tail-end portion, or the entirety of the proppant particulates may be coated. In certain embodiments, at least a majority of the proppant particulates are coated with curable resin and allowed to consolidate in-situ to form a hardenable mass.

[016] Alternatively, a tackifying agent could be used rather than a curable resin. If used, the tackifying agent is preferably but not necessarily incorporated with the proppant particulates before they are mixed with the degradable material. The tackifying agent, *inter alia*, helps distribute the degradable material within the proppant composition and keep it in place within the proppant matrix. Using a tackifier as opposed to a curable resin could be especially useful if the degradable material utilized has a low density or specific gravity or has a substantially different particle size than the proppant particulates. In one embodiment of the present invention, the tackifying agent is coated onto the proppant particulates early in the proppant stage of the fracturing treatment. Then, resin-coated proppant particulates are used during the tail-in stage of the fracturing treatment. In another embodiment, the tackifying agent and the curable resin are coated on the proppant particulates intermittently.

[017] In any event, to appreciate some of the beneficial effects of the present invention, the proppant particulates should consolidate within a fracture in the formation to form a proppant matrix. The term "proppant matrix" as used herein simply refers to a consolidation of proppant within a fracture adjacent to a wellbore in a subterranean formation. The mechanism by which the proppant matrix consolidates within the fracture is not important, *e.g.*, a curable resin, or a tackifying agent. Any suitable method can be used, including mechanical methods, *e.g.*, interlocking proppant particulates. Thus, in a preferred embodiment, the removal of the degradable material occurs after the proppant matrix has developed some substantial compressive strength or

stability inside the fracture to minimize shifting or rearrangement of proppant particulates within the pack.

[018] The degradable material is incorporated in the proppant composition and becomes distributed throughout the proppant matrix, most preferably uniformly, as the proppant matrix forms. After the requisite time period dictated by the characteristics of the particular degradable material utilized, the degradable material undergoes an irreversible degradation. This degradation, in effect, causes the degradable material to substantially be removed from the proppant matrix. As a result, voids are created in the proppant matrix. These voids enhance the permeability of the matrix, which results, *inter alia*, in enhanced conductivity. Enhanced fracture conductivity enhances well productivity, as well productivity is a function, *inter alia*, of fracture conductivity.

[019] Nonlimiting examples of degradable materials that may be used in conjunction with the present invention include but are not limited to degradable polymers, dehydrated salts, and/or mixtures of the two.

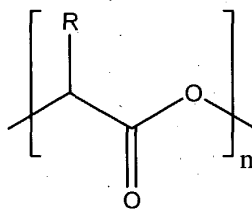
[020] As for degradable polymers, a polymer is considered to be "degradable" herein if the degradation is due to, *inter alia*, chemical and/or radical process such as hydrolysis, oxidation, or UV radiation. The degradability of a polymer depends at least in part on its backbone structure. For instance, the presence of hydrolyzable and/or oxidizable linkages in the backbone often yields a material that will degrade as described herein. The rates at which such polymers degrade are dependent on the type of repetitive unit, composition, sequence, length, molecular geometry, molecular weight, morphology (*e.g.*, crystallinity, size of spherulites, and orientation), hydrophilicity, hydrophobicity, surface area, and additives. Also, the environment to which the polymer is subjected may affect how it degrades, *e.g.*, temperature, presence of moisture, oxygen, microorganisms, enzymes, pH, and the like.

[021] Suitable examples of degradable polymers that may be used in accordance with the present invention include but are not limited to those described in the publication of Advances in Polymer Science, Vol. 157 entitled "Degradable Aliphatic Polyesters" edited by A.-C. Albertsson. Specific examples include homopolymers, random, block, graft, and star- and hyper-branched aliphatic polyesters.

Polycondensation reactions, ring-opening polymerizations, free radical polymerizations, anionic polymerizations, carbocationic polymerizations, coordinative ring-opening polymerization, and any other suitable process may prepare such suitable polymers. Specific examples of suitable polymers include polysaccharides such as dextran or cellulose; chitins; chitosans; proteins; aliphatic polyesters; poly(lactides); poly(glycolides); poly( $\epsilon$ -caprolactones); poly(hydroxybutyrates); poly(anhydrides); aliphatic polycarbonates; poly(orthoesters); poly(amino acids); poly(ethylene oxides); and polyphosphazenes. Of these suitable polymers, aliphatic polyesters and polyanhydrides are preferred.

[022] Aliphatic polyesters degrade chemically, *inter alia*, by hydrolytic cleavage. Hydrolysis can be catalyzed by either acids or bases. Generally, during the hydrolysis, carboxylic end groups are formed during chain scission, and this may enhance the rate of further hydrolysis. This mechanism is known in the art as "autocatalysis," and is thought to make polyester matrices more bulk eroding.

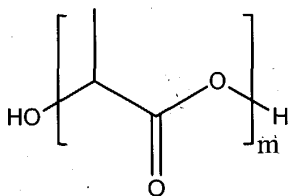
[023] Suitable aliphatic polyesters have the general formula of repeating units shown below:



Formula I

where n is an integer between 75 and 10,000 and R is selected from the group consisting of hydrogen, alkyl, aryl, alkylaryl, acetyl, heteroatoms, and mixtures thereof. Of the suitable aliphatic polyesters, poly(lactide) is preferred. Poly(lactide) is synthesized either from lactic acid by a condensation reaction or more commonly by ring-opening polymerization of cyclic lactide monomer. Since both lactic acid and lactide can achieve the same repeating unit, the general term poly(lactic acid) as used herein refers to formula I without any limitation as to how the polymer was made such as from lactides, lactic acid, or oligomers, and without reference to the degree of polymerization or level of plasticization.

[024] The lactide monomer exists generally in three different forms: two stereoisomers L- and D-lactide and racemic D,L-lactide (meso-lactide). The oligomers of lactic acid, and oligomers of lactide are defined by the formula:



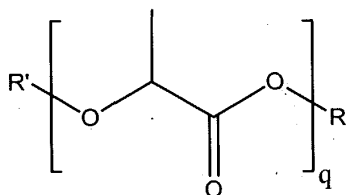
Formula II

where  $m$  is an integer  $2 \leq m \leq 75$ . Preferably  $m$  is an integer and  $2 \leq m \leq 10$ . These limits correspond to number average molecular weights below about 5,400 and below about 720, respectively. The chirality of the lactide units provides a means to adjust, *inter alia*, degradation rates, as well as physical and mechanical properties. Poly(L-lactide), for instance, is a semicrystalline polymer with a relatively slow hydrolysis rate. This could be desirable in applications of the present invention where a slower degradation of the degradable particulate is desired. Poly(D,L-lactide) may be a more amorphous polymer with a resultant faster hydrolysis rate. This may be suitable for other applications where a more rapid degradation may be appropriate. The stereoisomers of lactic acid may be used individually or combined to be used in accordance with the present invention. Additionally, they may be copolymerized with, for example, glycolide or other monomers like  $\epsilon$ -caprolactone, 1,5-dioxepan-2-one, trimethylene carbonate, or other suitable monomers to obtain polymers with different properties or degradation times. Additionally, the lactic acid stereoisomers can be modified to be used in the present invention by, *inter alia*, blending, copolymerizing or otherwise mixing the stereoisomers, blending, copolymerizing or otherwise mixing high and low molecular weight polylactides, or by blending, copolymerizing or otherwise mixing a polylactide with another polyester or polyesters.

[025] Plasticizers may be present in the polymeric degradable materials of the present invention. The plasticizers may be present in an amount sufficient to provide the desired characteristics, for example, (a) more effective compatibilization of the melt blend components, (b) improved processing characteristics during the blending



and processing steps, and (c) control and regulation of the sensitivity and degradation of the polymer by moisture. Suitable plasticizers include but are not limited to derivatives of oligomeric lactic acid, selected from the group defined by the formula:



Formula III

where R is a hydrogen, alkyl, aryl, alkylaryl, acetyl, heteroatom, or a mixture thereof and R is saturated, where R' is a hydrogen, alkyl, aryl, alkylaryl, acetyl, heteroatom, or a mixture thereof and R' is saturated, where R and R' cannot both be hydrogen, where q is an integer and  $2 \leq q \leq 75$ ; and mixtures thereof. Preferably q is an integer and  $2 \leq q \leq 10$ . As used herein the term "derivatives of oligomeric lactic acid" includes derivatives of oligomeric lactide. In addition to the other qualities above, the plasticizers may enhance the degradation rate of the degradable polymeric materials. The plasticizers, if used, are preferably at least intimately incorporated within the degradable polymeric materials.

[026] Aliphatic polyesters useful in the present invention may be prepared by substantially any of the conventionally known manufacturing methods such as those described in U.S. Patent Nos. 6,323,307; 5,216,050; 4,387,769; 3,912,692; and 2,703,316, the relevant disclosures of which are incorporated herein by reference.

[027] Polyanhydrides are another type of particularly suitable degradable polymer useful in the present invention. Polyanhydride hydrolysis proceeds, *inter alia*, via free carboxylic acid chain-ends to yield carboxylic acids as final degradation products. The erosion time can be varied over a broad range of changes in the polymer backbone. Examples of suitable polyanhydrides include poly(adipic anhydride), poly(suberic anhydride), poly(sebacic anhydride), and poly(dodecanedioic anhydride). Other suitable examples include but are not limited to poly(maleic anhydride) and poly(benzoic anhydride).

[028] The physical properties of degradable polymers depend on several factors such as the composition of the repeat units, flexibility of the chain, presence of

polar groups, molecular mass, degree of branching, crystallinity, orientation, etc. For example, short chain branches reduce the degree of crystallinity of polymers while long chain branches lower the melt viscosity and impart, *inter alia*, elongational viscosity with tension-stiffening behavior. The properties of the material utilized can be further tailored by blending, and copolymerizing it with another polymer, or by a change in the macromolecular architecture (e.g., hyper-branched polymers, star-shaped, or dendrimers, etc.). The properties of any such suitable degradable polymers (e.g., hydrophobicity, hydrophilicity, rate of degradation, etc.) can be tailored by introducing select functional groups along the polymer chains. For example, poly(phenyllactide) will degrade at about 1/5th of the rate of racemic poly(lactide) at a pH of 7.4 at 55°C. One of ordinary skill in the art with the benefit of this disclosure will be able to determine the appropriate degradable polymer to achieve the desired physical properties of the degradable polymers.

[029] Dehydrated salts may be used in accordance with the present invention as a degradable material. A dehydrated salt is suitable for use in the present invention if it will degrade over time as it hydrates. For example, a particulate solid anhydrous borate material that degrades over time may be suitable. Specific examples of particulate solid anhydrous borate materials that may be used include but are not limited to anhydrous sodium tetraborate (also known as anhydrous borax), and anhydrous boric acid. These anhydrous borate materials are only slightly soluble in water. However, with time and heat in a subterranean environment, the anhydrous borate materials react with the surrounding aqueous fluid and are hydrated. The resulting hydrated borate materials are highly soluble in water as compared to anhydrous borate materials and as a result degrade in the aqueous fluid. In some instances, the total time required for the anhydrous borate materials to degrade in an aqueous fluid is in the range of from about 8 hours to about 72 hours depending upon the temperature of the subterranean zone in which they are placed. Other examples include organic or inorganic salts like acetate trihydrate.

[030] Blends of certain degradable materials may also be suitable. One example of a suitable blend of materials is a mixture of poly(lactic acid) and sodium borate where the mixing of an acid and base could result in a neutral solution where this is desirable. Another example would include a blend of poly(lactic acid) and boric oxide.

Other materials that undergo an irreversible degradation may also be suitable, if the products of the degradation do not undesirably interfere with either the conductivity of the proppant matrix or with the production of any of the fluids from the subterranean formation.

[031] In choosing the appropriate degradable material, one should consider the degradation products that will result. These degradation products should not adversely affect other operations or components. The choice of degradable material also can depend, at least in part, on the conditions of the well, *e.g.*, wellbore temperature. For instance, lactides have been found to be suitable for lower temperature wells, including those within the range of 60°F to 150°F, and polylactides have been found to be suitable for well bore temperatures above this range. Also, poly(lactic acid) may be suitable for higher temperature wells. Some stereoisomers of poly(lactide) or mixtures of such stereoisomers may be suitable for even higher temperature applications. Dehydrated salts may also be suitable for higher temperature wells.

[032] Also, we have found that a preferable result is achieved if the degradable material degrades slowly over time as opposed to instantaneously. Even more preferable results have been obtained when the degradable material does not begin to degrade until after the proppant matrix has developed some compressive strength. The slow degradation of the degradable material, *inter alia*, helps to maintain the stability of the proppant matrix.

[033] If the application in which the degradable material will be used does not contain a component that will enable the degradable material to degrade, *e.g.*, in a dry gas hole, then in alternative embodiments of the present invention, the degradable material can be mixed with inorganic or organic compound to form what is referred to herein as a composite. In preferred alternative embodiments, the inorganic or organic compound in the composite is hydrated. Examples of the hydrated organic or inorganic solid compounds that can be utilized in the self-degradable diverting material include, but are not limited to, hydrates of organic acids or their salts such as sodium acetate trihydrate, L-tartaric acid disodium salt dihydrate, sodium citrate dihydrate, hydrates of inorganic acids or their salts such as sodium tetraborate decahydrate, sodium hydrogen phosphate heptahydrate, sodium phosphate dodecahydrate, amylose, starch-based

hydrophilic polymers, and cellulose-based hydrophilic polymers. Of these, sodium acetate trihydrate is preferred. The lactide units of the aliphatic polyester and the releasable water of the organic or inorganic solid compound utilized are preferably present in the mixture in equal molar amounts. The degradable material is then in a sense self-degradable, in that the degradable should at least partially degrade in the releasable water provided by the hydrated organic or inorganic compound which dehydrates over time when heated in the subterranean zone.

[034] The specific features of the degradable material may be chosen or modified to provide the proppant matrix with optimum conductivity while maintaining its desirable filtering capability. Preferably, the degradable material is selected to have a size, and shape similar to the size and shape of the curable proppant particulates to help maintain substantial uniformity within the mixture. It is preferable if the proppant particulates and the degradable material do not segregate within the proppant composition. Whichever degradable material is utilized, the degradable materials may have any shape, depending on the desired characteristics of the resultant voids in the proppant matrix including but not limited to particles having the physical shape of platelets, shavings, flakes, ribbons, rods, strips, spheroids, toroids, pellets, tablets, or any other physical shape. The physical shape of the degradable material should be chosen so as to enhance the desired shape and relative composition of the resultant voids within the proppant matrix. For example, a rod-like particle shape may be suitable in applications wherein channel-like voids in the proppant matrix are desired. One of ordinary skill in the art with the benefit of this disclosure will recognize the specific degradable material and the preferred size and shape for a given application.

[035] The proppant composition can either be pre-blended and then transported to the well site, or it can be prepared on-the-fly at the well site and then introduced downhole. Preferably, the proppant particles and the degradable material should be mixed so as to form a uniform cohesive mixture in the fracturing treatment fluid. Any conventional fracturing fluid may be used in accordance with the present invention.

[036] The concentration of the degradable material in the proppant composition ranges from about 0.1% to about 30%, based on the weight of the proppant

in the mixture. A concentration of degradable material between about 1% and about 5% by weight of the proppant is preferable. Additionally, the relative amounts of the degradable material in the proppant composition should not be such that when degraded, an undesirable percentage of voids result in the proppant matrix making the proppant matrix potentially ineffective in maintaining the integrity of the fracture. One of ordinary skill in the art with the benefit of this disclosure will recognize an optimum concentration of degradable material that provides desirable values in terms of enhanced conductivity or permeability without undermining the stability of the proppant pack itself.

[037] To facilitate a better understanding of the present invention, the following examples of preferred embodiments are given. In no way should such examples be read to limit the scope of the invention.

#### **EXAMPLES**

[038] Proppant matrixes were formed by mixing 20/40-mesh bauxite proppant with various amounts of degradable material, specifically polylactic acid. 250 grams of proppant was first coated with 11 ml of a curable epoxy resin. Polylactic acid particulates were then added to the resin-coated proppant and blended thoroughly to form a homogeneous blend. The amounts of polylactic acid added to each composition were 0%, 5%, and 10% and 20% by weight of the proppant particulates in the composition. Mixing the mixture with water formed a slurry. The slurry was then packed into a brass flow cell and placed in an oven to be cured under a 500-psi stress load at 275°F for 4 days. After this curing period, permeability testing was performed for the consolidated proppant matrixes. Table 1 reports the resulting permeability values obtained for the proppant matrixes.

**TABLE 1**

| <b>Amount of Polylactic Acid Particulate<br/>Added to the Proppant (weight %)</b> | <b>Proppant Pack Permeability<br/>(Darcies)</b> |
|-----------------------------------------------------------------------------------|-------------------------------------------------|
| 0                                                                                 | 52                                              |
| 5                                                                                 | 100                                             |
| 10                                                                                | 163                                             |
| 20                                                                                | 167                                             |

[039] As can be seen from Table 1, the permeability of the proppant matrix was enhanced by the addition of the degradable material, specifically polylactic acid particulate. This enhancement increased with the percentage by weight of the degradable material utilized.

[040] Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit and scope of this invention as defined by the appended claims.

What is claimed is:

1. A method of increasing the conductivity of a fracture in a subterranean formation comprising the steps of:
  - providing a fracturing treatment fluid comprising a proppant composition, the proppant composition comprising proppant particulates and a degradable material capable of undergoing an irreversible degradation downhole;
  - introducing the proppant composition to the fracture; and
  - allowing the proppant composition to form a proppant matrix having voids in the fracture.
2. The method of claim 1 wherein the proppant particulates comprise sand, walnut hulls, or a man-made proppants.
3. The method of claim 1 wherein the proppant particulates have a size of 10 to 60 US mesh.
4. The method of claim 1 wherein the proppant composition further comprises a curable resin, a tackifying agent, or both.
5. The method of claim 4 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.
6. The method of claim 1 wherein the proppant composition comprises interlocking proppant.
7. The method of claim 1 wherein the degradable material comprises a degradable polymer or a dehydrated salt.
8. The method of claim 7 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.
9. The method of claim 1 wherein the degradable material further comprises a plasticizer.
10. The method of claim 7 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

11. The method of claim 1 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.
12. The method of claim 1 wherein the degradable material comprises a stereoisomer of a poly(lactide).
13. The method of claim 1 wherein the proppant composition comprises a bauxite proppant, the bauxite proppant having been coated with a curable epoxy resin, and a polylactic acid degradable material.
14. The method of claim 1 wherein the degradable material is present in the proppant composition in an amount sufficient to create a desirable number of voids in the proppant matrix.
15. The method of claim 1 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the composition.
16. The method of claim 1 wherein the degradable material comprises particles having a rod-like shape.
17. The method of claim 1 wherein the degradable material comprises an inorganic or organic compound.
18. The method of claim 17 wherein the inorganic or organic compound comprises sodium acetate trihydrate, L-tartaric acid disodium, salt dihydrate, sodium citrate dihydrate, hydrate of an inorganic acid, hydrate of an inorganic acid salt, sodium tetraborate decahydrate, sodium hydrogenphosphate heptahydrate, sodium phosphate, dodecahydrate, amylose, starch-based hydrophilic polymer, or a cellulose-based hydrophilic polymer.
19. The method of claim 1 wherein the degradable material is a composite.
20. A method of enhancing the permeability of a proppant matrix comprising the step of introducing voids into the proppant matrix by a degradation of a degradable material within the matrix.
21. The method of claim 20 wherein the proppant matrix comprises sand, walnut hulls, or a man-made proppant particulates.



22. The method of claim 20 wherein the proppant matrix comprises a curable resin, a tackifying agent, or both.

23. The method of claim 22 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.

24. The method of claim 20 wherein the proppant matrix comprises interlocking proppant particulates.

25. The method of claim 20 wherein the degradable material comprises a degradable polymer or a dehydrated salt.

26. The method of claim 25 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.

27. The method of claim 20 wherein the degradable material further comprises a plasticizer.

28. The method of claim 25 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

29. The method of claim 20 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

30. The method of claim 20 wherein the degradable material comprises a stereoisomer of a poly(lactide).

31. The method of claim 20 wherein the proppant matrix comprises a bauxite proppant particulates, the bauxite proppant particulates having been coated with a curable epoxy resin, and a polylactic acid degradable material.

32. The method of claim 20 wherein the degradable material is present in the proppant matrix in an amount sufficient to create a desirable number of voids in the proppant matrix.

33. The method of claim 20 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the composition.

34. The method of claim 20 wherein the degradable material comprises particles having a rod-like shape.
35. The method of claim 20 wherein the at least a portion of the voids in the proppant matrix are channel-like in shape.
36. A proppant composition comprising:  
proppant particulates, and  
a degradable material that undergoes an irreversible degradation downhole.
37. The composition of claim 36 wherein the proppant particulates comprise sand, walnut hulls, or a man-made proppant particulates.
38. The composition of claim 36 wherein the proppant particulates have a size of 10 to 60 US mesh.
39. The composition of claim 36 wherein the proppant composition further comprises a curable resin, a tackifying agent, or both.
40. The composition of claim 39 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.
41. The composition of claim 36 wherein the proppant composition comprises interlocking proppant particulates.
42. The composition of claim 36 wherein the degradable material comprises a degradable polymer or a dehydrated salt.
43. The composition of claim 42 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.
44. The composition of claim 36 wherein the degradable material further comprises a plasticizer.
45. The composition of claim 42 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

46. The composition of claim 36 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

47. The composition of claim 36 wherein the degradable material comprises a stereoisomer of a poly(lactide).

48. The composition of claim 36 wherein the proppant composition comprises a bauxite proppant particulates, the bauxite proppant particulates having been coated with a curable epoxy resin, and a polylactic acid degradable material.

49. The composition of claim 36 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of the particulates in the composition.

50. The composition of claim 36 wherein the degradable material comprises particles having a rod-like shape.

51. The composition of claim 36 wherein the degradable material comprises an inorganic or organic compound.

52. The composition of claim 37 wherein the inorganic or organic compound comprises sodium acetate trihydrate, L-tartaric acid disodium, salt dihydrate, sodium citrate dihydrate, hydrate of an inorganic acid, hydrate of an inorganic acid salt, sodium tetraborate decahydrate, sodium hydrogenphosphate heptahydrate, sodium phosphate, dodecahydrate, amylose, starch-based hydrophilic polymer, or a cellulose-based hydrophilic polymer.

53. The composition of claim 36 wherein the degradable material is a composite.

54. A composition for enhancing the permeability of a proppant matrix comprising proppant particulates and a degradable material.

55. The composition of claim 54 wherein the proppant particulates comprise sand, walnut hulls, or a man-made proppant particulates.

56. The composition of claim 54 wherein the proppant particulates have a size of 10 to 60 US mesh.

57. The composition of claim 54 wherein the proppant composition further comprises a curable resin, a tackifying agent, or both.

58. The composition of claim 57 wherein the curable resin comprises an epoxy, furan, phenolic, furfuryl aldehyde, or furfuryl alcohol resin.

59. The composition of claim 54 wherein the proppant composition comprises interlocking proppant particulates.

60. The composition of claim 54 wherein the degradable material comprises a degradable polymer or a dehydrated salt.

61. The composition of claim 60 wherein the degradable polymer comprises polysaccharides, chitins, chitosans, proteins, aliphatic polyesters, poly(lactides), poly(glycolides), poly( $\epsilon$ -caprolactones), poly(hydroxybutyrates), polyanhydrides, aliphatic polycarbonates, poly(orthoesters), poly(amino acids); poly(ethylene oxides), or polyphosphazenes.

62. The composition of claim 54 wherein the degradable material further comprises a plasticizer.

63. The composition of claim 60 wherein the dehydrated salt comprises anhydrous sodium tetraborate or anhydrous boric acid.

64. The composition of claim 54 wherein the degradable material comprises poly(lactic acid) and a compound chosen from the group consisting of sodium borate and boric oxide.

65. The composition of claim 54 wherein the degradable material comprises a stereoisomer of a poly(lactide).

66. The composition of claim 54 wherein the proppant composition comprises a bauxite proppant particulates, the bauxite proppant particulates having been coated with a curable epoxy resin, and a polylactic acid degradable material.

67. The composition of claim 54 wherein the degradable material is present in the proppant composition in an amount of about 0.1% to about 30% by weight of proppant particulates in the proppant composition.

68. The composition of claim 54 wherein the degradable material comprises particles having a rod-like shape.

**COMPOSITIONS AND METHODS FOR IMPROVING PROPPANT PACK  
PERMEABILITY AND FRACTURE CONDUCTIVITY  
IN A SUBTERRANEAN WELL**

**ABSTRACT**

[041] The present invention relates to enhancing fluid flow from subterranean formations. More particularly, this invention relates to providing improved proppant matrixes within fractures in a subterranean formation. An example of the methods of increasing the conductivity of a fracture in a subterranean formation comprises the steps of providing a fracturing treatment fluid comprising a proppant composition, the proppant composition comprising proppant particulates and a degradable material capable of undergoing an irreversible degradation downhole; introducing the proppant composition to the fracture; and allowing the proppant composition to form a proppant matrix having voids in the fracture.

**DECLARATION FOR UTILITY OR  
DESIGN  
PATENT APPLICATION  
(37 CFR 1.63)**

☒ Declaration Submitted with Initial Filing  
OR  
☐ Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number 2002-IP-009210U1

First Named Inventor Philip D. Nguyen, et al

**COMPLETE IF KNOWN**

Application Number

Filing Date

Art Unit

Examiner Name

22002 U.S. PTO  
10/608991

06/27/03

As the below named inventor, I hereby declare that:

My residence, mailing address, and citizenship are as stated below next to my name.

I believe I am the original and first inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Compositions and Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean Well

(Title of the Invention)

the specification of which

☒ is attached hereto

OR

☐ was filed on (MM/DD/YYYY)

as United States Application Number or PCT International

Application Number and was amended on (MM/DD/YYYY) (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY) | Priority Not Claimed     | Certified Copy Attached? |                          |
|-------------------------------------|---------|----------------------------------|--------------------------|--------------------------|--------------------------|
|                                     |         |                                  |                          | YES                      | NO                       |
|                                     |         |                                  | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
|                                     |         |                                  | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
|                                     |         |                                  | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
|                                     |         |                                  | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |

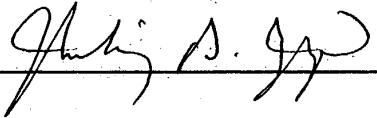
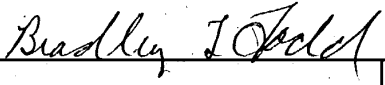
☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

[Page 1 of 2]

Burden Hour Statement: This form is estimated to take 21 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

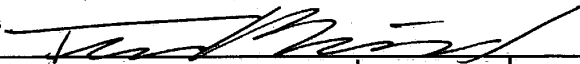
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

**DECLARATION — Utility or Design Patent Application**

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                                                                               |                    |                                                                     |  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|-------------------------------------------------------------------------------|--------------------|---------------------------------------------------------------------|--|
| Direct all correspondence to: <input checked="" type="checkbox"/>                                                                                                                                                                                                                                                                                                                                                                                                         |  | Customer Number<br>or Bar Code Label                                          |                    | OR <input checked="" type="checkbox"/> Correspondence address below |  |
| Robert A. Kent                                                                                                                                                                                                                                                                                                                                                                                                                                                            |  |                                                                               |                    |                                                                     |  |
| Name                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |                                                                               |                    |                                                                     |  |
| Halliburton Energy Services                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |                                                                               |                    |                                                                     |  |
| Address P.O. Box 1431                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |                                                                               |                    |                                                                     |  |
| Duncan                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | OK                                                                            |                    | 73536-0440                                                          |  |
| City                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  | State                                                                         |                    | ZIP                                                                 |  |
| USA                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |  | 580-251-3125                                                                  |                    | 580-251-3917                                                        |  |
| Country                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  | Telephone                                                                     |                    | Fax                                                                 |  |
| I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon. |  |                                                                               |                    |                                                                     |  |
| NAME OF SOLE OR FIRST INVENTOR :                                                                                                                                                                                                                                                                                                                                                                                                                                          |  | <input type="checkbox"/> A petition has been filed for this unsigned inventor |                    |                                                                     |  |
| Given Name Philip D.<br>(first and middle [if any])                                                                                                                                                                                                                                                                                                                                                                                                                       |  |                                                                               | Family Name Nguyen |                                                                     |  |
| Inventor's Signature                                                                                                                                                                                                                                                                                                                                                                   |  |                                                                               | Date 6/12/03       |                                                                     |  |
| Duncan                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | OK                                                                            |                    | USA                                                                 |  |
| Residence: City                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  | State                                                                         |                    | Country                                                             |  |
| 1107 W. Jones Ave.                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |                                                                               |                    | US                                                                  |  |
| Mailing Address                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                                                                               |                    | Citizenship                                                         |  |
| Duncan                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | OK                                                                            |                    | 73533                                                               |  |
| City                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  | State                                                                         |                    | ZIP                                                                 |  |
| USA                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |  |                                                                               |                    | Country                                                             |  |
| NAME OF SECOND INVENTOR:                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  | <input type="checkbox"/> A petition has been filed for this unsigned inventor |                    |                                                                     |  |
| Given Name Bradley L.<br>(first and middle [if any])                                                                                                                                                                                                                                                                                                                                                                                                                      |  |                                                                               | Family Name Todd   |                                                                     |  |
| Inventor's Signature                                                                                                                                                                                                                                                                                                                                                                   |  |                                                                               | Date 6/12/03       |                                                                     |  |
| Duncan                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | OK                                                                            |                    | USA                                                                 |  |
| Residence: City                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  | State                                                                         |                    | Country                                                             |  |
| 1810 Windsor Drive                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |                                                                               |                    | US                                                                  |  |
| Mailing Address                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                                                                               |                    | Citizenship                                                         |  |
| Duncan                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | OK                                                                            |                    | 73533                                                               |  |
| City                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  | State                                                                         |                    | ZIP                                                                 |  |
| USA                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |  |                                                                               |                    | Country                                                             |  |
| <input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto.                                                                                                                                                                                                                                                                                                         |  |                                                                               |                    |                                                                     |  |

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**DECLARATION****ADDITIONAL INVENTOR(S)**  
**Supplemental Sheet**  
Page 1 of 1

|                                                                                                        |             |                                                                               |                   |
|--------------------------------------------------------------------------------------------------------|-------------|-------------------------------------------------------------------------------|-------------------|
| <b>Name of Additional Joint Inventor, if any:</b>                                                      |             | <input type="checkbox"/> A petition has been filed for this unsigned inventor |                   |
| Trinidad<br>Given Name                                                                                 |             | Munoz Jr.<br>Family Name or Surname                                           |                   |
| Inventor's Signature  |             | Date 6/2-03                                                                   |                   |
| Duncan<br>Residence: City                                                                              | OK<br>State | USA<br>Country                                                                | US<br>Citizenship |
| 701 Drexal Place<br>Mailing Address                                                                    |             |                                                                               |                   |
| Mailing Address                                                                                        |             |                                                                               |                   |
| Duncan<br>City                                                                                         | OK<br>State | 73533<br>ZIP                                                                  | USA<br>Country    |
| <b>Name of Additional Joint Inventor, if any:</b>                                                      |             | <input type="checkbox"/> A petition has been filed for this unsigned inventor |                   |
| Given Name                                                                                             |             | Family Name or Surname                                                        |                   |
| Inventor's Signature                                                                                   |             | Date                                                                          |                   |
| Residence: City                                                                                        | State       | Country                                                                       | Citizenship       |
| Mailing Address                                                                                        |             |                                                                               |                   |
| Mailing Address                                                                                        |             |                                                                               |                   |
| City                                                                                                   | State       | ZIP                                                                           | Country           |
| <b>Name of Additional Joint Inventor, if any:</b>                                                      |             | <input type="checkbox"/> A petition has been filed for this unsigned inventor |                   |
| Given Name                                                                                             |             | Family Name or Surname                                                        |                   |
| Inventor's Signature                                                                                   |             | Date                                                                          |                   |
| Residence: City                                                                                        | State       | Country                                                                       | Citizenship       |
| Mailing Address                                                                                        |             |                                                                               |                   |
| Mailing Address                                                                                        |             |                                                                               |                   |
| City                                                                                                   | State       | ZIP                                                                           | Country           |

Burden Hour Statement: This form is estimated to take 21 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.



Please type a plus sign (+) inside this box → ☐

PTO/SB/02C (3-97)

Approved for use through 8/30/98. OMB 0851-0032

Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

| DECLARATION                                     |                     | REGISTERED PRACTITIONER INFORMATION<br>(Supplemental Sheet) |                     |
|-------------------------------------------------|---------------------|-------------------------------------------------------------|---------------------|
| Name                                            | Registration Number | Name                                                        | Registration Number |
| Halliburton Energy Services, Inc. Practitioners |                     | Baker Botts Practitioners                                   |                     |
| William E. Shull                                | 29,438              | Scott F. Partridge                                          | 28,142              |
| Michael D. McCully                              | 29,566              | Mitchell D. Lukin                                           | 30,772              |
| Mark A. Smith                                   | 30,220              | Claude E. Cooke, Jr.                                        | 34,142              |
| William M. Imwalle                              | 35,904              | Paul N. Katz                                                | 35,917              |
| Paul I. Herman                                  | 37,349              | Ronald L. Chichester                                        | 36,765              |
| Robert A. Kent                                  | 28,626              | Howard Speight                                              | 37,733              |
| Craig W. Roddy                                  | 36,256              | Michael Hawes                                               | 38,487              |
| John W. Wustenberg                              | 35,415              | Roger J. Fulghum                                            | 39,678              |
|                                                 |                     | Michael Locklar                                             | 44,878              |
|                                                 |                     | Carey C. Jordan                                             | 47,646              |
|                                                 |                     | John Shumaker                                               | 52,223              |
|                                                 |                     | David C. Sulkis                                             | 52,260              |

**Estimated Hour Statement:** This form is estimated to take 8.4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20501. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20501.

Declaration — Registered Practitioner Information (Supplemental Sheet) (PTO/SB/02C)(1-1.4)

Please type a plus sign (+) inside this box → ☐

PTO/SB/81 (02-01)

Approved for use through 10/31/2002. OMB 0651-0035

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

## POWER OF ATTORNEY OR AUTHORIZATION OF AGENT

Application Number

Filing Date

First Named Inventor

Philip D. Nguyen, et al

Title

Compositions and Methods

Group Art Unit

Examiner Name

Attorney Docket Number

2002-IP-009210U1

I hereby appoint:

☒ Practitioners at Customer Number

OR

☐ Practitioner(s) named below:

| Name         | Registration Number |
|--------------|---------------------|
| See attached |                     |
|              |                     |
|              |                     |

Place Customer  
Number Bar Code  
Label here

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the United States Patent and Trademark Office connected therewith.

Please change the correspondence address for the above-identified application to:

☐ The above-mentioned Customer Number.

OR

☐ Practitioners at Customer Number

OR

Place Customer  
Number Bar Code  
Label here

☐ Firm or  
Individual Name

Address

Address

City

State

Zip

Country

Telephone

Fax

I am the:

☐ Applicant/Inventor.

☒ Assignee of record of the entire interest. See 37 CFR 3.71.

Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

### SIGNATURE of Applicant or Assignee of Record

|           |                       |
|-----------|-----------------------|
| Name      | Robert A. Kent        |
| Signature | <i>Robert A. Kent</i> |
| Date      | 6-25-03               |

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below\*.

☐ \*Total of \_\_\_\_\_ forms are submitted.

Burden Hour Statement: This form is estimated to take 3 minutes to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DONOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

**STATEMENT UNDER 37 CFR 3.73(b)**Applicant/Patent Owner: Philip D. Nguyen, et alApplication No./Patent No.: Unknown Filed/Issue Date: Concurrently HerewithEntitled: Compositions and Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean WellHalliburton Energy Services, Inc., a corporation

(Name of Assignee)

(Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that it is:

1. ☒ the assignee of the entire right, title, and interest; or
2. ☐ an assignee of less than the entire right, title and interest.  
The extent (by, percentage) of its ownership interest is \_\_\_\_\_ %
- in the patent application/patent identified above by virtue of either:

A. ☒ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel \_\_\_\_\_, Frame \_\_\_\_\_, or for which a copy thereof is attached.

OR

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as shown below:

1. From: \_\_\_\_\_ To: \_\_\_\_\_  
The document was recorded in the United States Patent and Trademark Office at Reel \_\_\_\_\_, Frame \_\_\_\_\_, or for which a copy thereof is attached.
2. From: \_\_\_\_\_ To: \_\_\_\_\_  
The document was recorded in the United States Patent and Trademark Office at Reel \_\_\_\_\_, Frame \_\_\_\_\_, or for which a copy thereof is attached.
3. From: \_\_\_\_\_ To: \_\_\_\_\_  
The document was recorded in the United States Patent and Trademark Office at Reel \_\_\_\_\_, Frame \_\_\_\_\_, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet.

☒ Copies of assignments or other documents in the chain of title are attached.

**[NOTE:** A separate copy (i.e., the original assignment document or a true copy of the original document) must be submitted to Assignment Division in accordance with 37 CFR Part 3, if the assignment is to be recorded in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

6-25-03

Date

Robert A. Kent

Typed or printed name

Robert A. Kent

Signature

Senior Counsel

Title

**Burden Hour Statement:** This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

# PATENT APPLICATION FEE DETERMINATION RECORD

Effective January 1, 2003

Application or Docket Number

10608291

## CLAIMS AS FILED - PART I

|                                                           | (Column 1)      | (Column 2)   |
|-----------------------------------------------------------|-----------------|--------------|
| TOTAL CLAIMS                                              | 68              |              |
| FOR                                                       | NUMBER FILED    | NUMBER EXTRA |
| TOTAL CHARGEABLE CLAIMS                                   | 68 minus 20 = * | 48           |
| INDEPENDENT CLAIMS                                        | 4 minus 3 = *   | 1            |
| MULTIPLE DEPENDENT CLAIM PRESENT <input type="checkbox"/> |                 |              |

\* If the difference in column 1 is less than zero, enter "0" in column 2

## CLAIMS AS AMENDED - PART II

|                                                                         | (Column 1)                       | (Column 2)                         | (Column 3)    |
|-------------------------------------------------------------------------|----------------------------------|------------------------------------|---------------|
| AMENDMENT A                                                             | CLAIMS REMAINING AFTER AMENDMENT | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA |
| Total                                                                   | *                                | Minus **                           | =             |
| Independent                                                             | *                                | Minus ***                          | =             |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM <input type="checkbox"/> |                                  |                                    |               |

20 36 54

|                                                                         | (Column 1)                       | (Column 2)                         | (Column 3)    |
|-------------------------------------------------------------------------|----------------------------------|------------------------------------|---------------|
| AMENDMENT B                                                             | CLAIMS REMAINING AFTER AMENDMENT | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA |
| Total                                                                   | *                                | Minus **                           | =             |
| Independent                                                             | *                                | Minus ***                          | =             |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM <input type="checkbox"/> |                                  |                                    |               |

|                                                                         | (Column 1)                       | (Column 2)                         | (Column 3)    |
|-------------------------------------------------------------------------|----------------------------------|------------------------------------|---------------|
| AMENDMENT C                                                             | CLAIMS REMAINING AFTER AMENDMENT | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA |
| Total                                                                   | *                                | Minus **                           | =             |
| Independent                                                             | *                                | Minus ***                          | =             |
| FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM <input type="checkbox"/> |                                  |                                    |               |

\* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

\*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20."

\*\*\* If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3."

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

## SMALL ENTITY TYPE

| RATE      | FEE    |
|-----------|--------|
| BASIC FEE | 375.00 |
| X\$9=     |        |
| X42=      |        |
| +140=     |        |
| TOTAL     |        |

| RATE      | FEE    |
|-----------|--------|
| BASIC FEE | 750.00 |
| X\$18=    | 864    |
| X84=      | 84     |
| +280=     |        |
| TOTAL     | 1698   |

## SMALL ENTITY

| RATE             | ADDITIONAL FEE |
|------------------|----------------|
| X\$9=            |                |
| X42=             |                |
| +140=            |                |
| TOTAL ADDIT. FEE |                |

| RATE             | ADDITIONAL FEE |
|------------------|----------------|
| X\$18=           |                |
| X84=             |                |
| +280=            |                |
| TOTAL ADDIT. FEE |                |

| RATE             | ADDITIONAL FEE |
|------------------|----------------|
| X\$9=            |                |
| X42=             |                |
| +140=            |                |
| TOTAL ADDIT. FEE |                |

| RATE             | ADDITIONAL FEE |
|------------------|----------------|
| X\$18=           |                |
| X84=             |                |
| +280=            |                |
| TOTAL ADDIT. FEE |                |

| RATE             | ADDITIONAL FEE |
|------------------|----------------|
| X\$9=            |                |
| X42=             |                |
| +140=            |                |
| TOTAL ADDIT. FEE |                |

| RATE             | ADDITIONAL FEE |
|------------------|----------------|
| X\$18=           |                |
| X84=             |                |
| +280=            |                |
| TOTAL ADDIT. FEE |                |

PATENT APPLICATION SERIAL NO. \_\_\_\_\_

U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE  
FEE RECORD SHEET

07/02/2003 SDIRETA1 00000020 080300 10608291

|            |           |
|------------|-----------|
| 01 FC:1001 | 750.00 DA |
| 02 FC:1202 | 864.00 DA |
| 03 FC:1201 | 84.00 DA  |

PTO-1556  
(5/87)

10608291

Sheet 1 of 2

|                                                                                                                                                                         |                                      |                       |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|-----------------------|
| <b>FORM PTO-1449 (Modified)</b><br><br>LIST OF PATENTS AND PUBLICATIONS<br>FOR APPLICANT'S INFORMATION<br>DISCLOSURE STATEMENT<br><br>(Use several sheets if necessary) | ATTY. DOCKET NO.<br>2002-IP-009210U1 | SERIAL NO.<br>Unknown |
|                                                                                                                                                                         | APPLICANT<br>Philip D. Nguyen, et al |                       |
|                                                                                                                                                                         | FILING DATE<br>Concurrently Herewith | GROUP<br>Unknown      |

## U.S. PATENT DOCUMENTS

| EXAMINER<br>INITIAL |    | Document No. | Date     | Name               | Class | Subclass | Filing<br>Date if<br>Appropriate |
|---------------------|----|--------------|----------|--------------------|-------|----------|----------------------------------|
|                     | AA | 4,387,769    | 06/14/83 | Erbstoesser, et al | 507   | 219      |                                  |
|                     | AB | 4,526,695    | 07/02/85 | Erbstoesser, et al | 507   | 219      |                                  |
|                     | AC | 6,172,011    | 01/09/01 | Card, et al        | 507   | 204      |                                  |
|                     | AD | 5,924,488    | 07/20/99 | Nguyen, et al      | 166   | 280      |                                  |
|                     | AE | 6,209,643    | 04/03/01 | Nguyen, et al      | 166   | 276      |                                  |
|                     | AF | 6,047,772    | 04/11/00 | Weaver, et al      | 166   | 276      |                                  |
|                     | AG | 5,908,073    | 06/01/99 | Nguyen, et al      | 166   | 276      |                                  |
|                     | AH | 5,791,415    | 08/11/98 | Nguyen, et al      | 166   | 280      |                                  |
|                     | AI | 4,694,905    | 09/22/87 | Armbruster         | 166   | 280      |                                  |
|                     | AJ | 4,785,884    | 11/22/88 | Armbruster         | 166   | 280      |                                  |
|                     | AK | 4,986,355    | 01/22/91 | Casad, et al       | 166   | 295      |                                  |

## FOREIGN PATENT DOCUMENTS

|  |    | Document No. | Date | Country | Class | Subclass | Translation |    |
|--|----|--------------|------|---------|-------|----------|-------------|----|
|  |    |              |      |         |       |          | Yes         | No |
|  | AL |              |      |         |       |          |             |    |
|  | AM |              |      |         |       |          |             |    |

## OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)

|  |    |                                                                                                                                                                                                       |
|--|----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | AN | "Poly(phenyllactide): Synthesis, Characterization, and Hydrolytic Degradation" published in Biomacromolecules, Vol. 2, No. 3, 2001, pages 658-663 by Tara L. Simmons and Gregory L. Baker.            |
|  | AO | "Synthesis and Properties of Polymers Derived from Substituted Lactic Acids" published in 2001 American Chemical Society, Chapter 12, pages 147-159 by Mao Yin, Tara L. Simmons and Gregory L. Baker. |
|  | AP | "Preparation and Characterization of Substituted Polylactides" published in 199 American Chemical Society, Volume 32, Number 23, pages 7711-7718 by Mao Yin and Gregory L. Baker.                     |

EXAMINER

DATE CONSIDERED

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

|                                                                                                                                                                         |                                      |                       |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|-----------------------|
| <b>FORM PTO-1449</b> (Modified)<br><br>LIST OF PATENTS AND PUBLICATIONS<br>FOR APPLICANT'S INFORMATION<br>DISCLOSURE STATEMENT<br><br>(Use several sheets if necessary) | ATTY. DOCKET NO.<br>2002-IP-009210U1 | SERIAL NO.<br>Unknown |
|                                                                                                                                                                         | APPLICANT<br>Philip D. Nguyen, et al |                       |
|                                                                                                                                                                         | FILING DATE<br>Concurrently Herewith | GROUP<br>Unknown      |

## U.S. PATENT DOCUMENTS

| EXAMINER<br>INITIAL |    | Document No. | Date     | Name          | Class | Subclass | Filing<br>Date if<br>Appropriate |
|---------------------|----|--------------|----------|---------------|-------|----------|----------------------------------|
|                     | AA | 4,715,967    | 12/29/87 | Bellis, et al | 252   | 8.551    |                                  |
|                     | AB | 4,886,354    | 12/12/89 | Welch, et al  | 356   | 70       |                                  |
|                     | AC | 4,986,353    | 01/22/91 | Clark, et al  | 166   | 279      |                                  |
|                     | AD | 4,957,165    | 09/18/90 | Cantu, et al  | 166   | 295      |                                  |
|                     | AE | 4,848,467    | 07/18/89 | Cantu, et al  | 166   | 281      |                                  |
|                     | AF | 3,960,736    | 06/01/76 | Free, et al   | 252   | 8.55     |                                  |
|                     | AG | 5,216,050    | 06/01/93 | Sinclair      | 524   | 108      |                                  |
|                     | AH | 6,323,307    | 11/27/01 | Bigg, et al   | 528   | 354      |                                  |
|                     | AI |              |          |               |       |          |                                  |
|                     | AJ |              |          |               |       |          |                                  |
|                     | AK |              |          |               |       |          |                                  |

## FOREIGN PATENT DOCUMENTS

|  | Document No. | Date | Country | Class | Subclass | Translation |    |
|--|--------------|------|---------|-------|----------|-------------|----|
|  |              |      |         |       |          | Yes         | No |
|  | AL           |      |         |       |          |             |    |
|  | AM           |      |         |       |          |             |    |

## OTHER ART (Including Author, Title, Date, Pertinent Pages, Etc.)

|          |    |  |  |                 |  |  |  |
|----------|----|--|--|-----------------|--|--|--|
|          | AN |  |  |                 |  |  |  |
|          | AO |  |  |                 |  |  |  |
|          | AP |  |  |                 |  |  |  |
| EXAMINER |    |  |  | DATE CONSIDERED |  |  |  |

EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

40608291

6/27/03

Docket No. HES 2002-IP-009210U1

#### ASSIGNMENT

Whereas, I/We, **Philip D. Nguyen, Bradley L. Todd and Trinidad Munoz, Jr.** of Stephens County, Duncan, Oklahoma, have invented **"Compositions and Methods for Improving Proppant Pack Permeability and Fracture Conductivity in a Subterranean Well"** for which I have made application for Letters Patent of the United States; and

Whereas, HALLIBURTON ENERGY SERVICES, INC., a Delaware Corporation, having a place of business at 10200 Bellaire Boulevard, Houston, Texas 77072 is desirous of acquiring an interest therein;

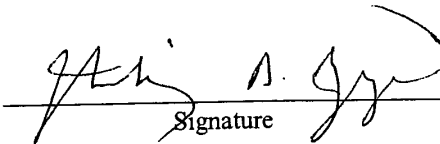
NOW, THEREFORE, in consideration of the sum of ten dollars (\$10.00) and other good and valuable consideration, the receipt and sufficiency of which is hereby acknowledged, I/We, by these presents do sell, assign and transfer and convey unto HALLIBURTON ENERGY SERVICES, INC., its successors and assigns, the full and exclusive right, for the United States of America and its territorial possessions and for any and all foreign countries, in and to the said invention, described in the Patent Application first executed on June 12, 2003, submitted concurrently herewith, and any divisional, continuing or reissue application based on the present application preparatory to obtaining Letters Patent of the United States therefor; said invention, application and any and all Letters Patent issuing therefor to be held and enjoyed by HALLIBURTON ENERGY SERVICES, INC., for its own use and behoof, and for its legal representatives, successors and assigns, to the full end of the term for which said Letters Patent may be granted, as fully and entirely as the same would have been held by me and had this assignment and sale not been made.

And I do further agree to sign all papers, make all rightful oaths and do all requisite acts for the filing of any disclaimer or for the filing and assignment of any divisional, continuing or reissue application or applications for patent based on the present application, as well as for any other U.S. or foreign application for patent which relates to the said invention.

And I do further agree to communicate to HALLIBURTON ENERGY SERVICES, INC., its successors, assign or other legal representatives, such facts relating to the invention disclosed in the present application or Letters Patent issuing thereon as may be known to me, and to testify as to such facts in any interference or other litigation.



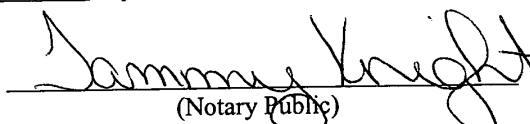
Executed this 12<sup>th</sup> day of June, 2003, at Duncan, Stephens County, Oklahoma U.S.A.

  
\_\_\_\_\_  
Signature

State of Oklahoma     )  
                                  ) ss  
County of Stephens    )

Before me personally appeared said **Philip D. Nguyen** and acknowledged the foregoing instrument to be his free act and deed this 12<sup>th</sup> day of June, 2003.

Seal  
2-13-2006

  
\_\_\_\_\_  
(Notary Public)  
#02002595

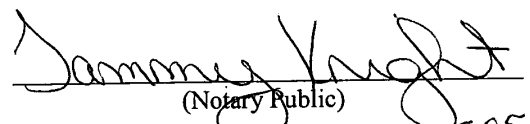
Executed this 12<sup>th</sup> day of June, 2003, at Duncan, Stephens County, Oklahoma U.S.A.

  
\_\_\_\_\_  
Signature


State of Oklahoma     )  
                                  ) ss  
County of Stephens    )

Before me personally appeared said **Bradley L. Todd** and acknowledged the foregoing instrument to be his free act and deed this 12<sup>th</sup> day of June, 2003.

Seal  
2-13-2006

  
\_\_\_\_\_  
(Notary Public)  
#02002595

Executed this 12<sup>th</sup> day of June, 2003, at Duncan, Stephens County, Oklahoma U.S.A.

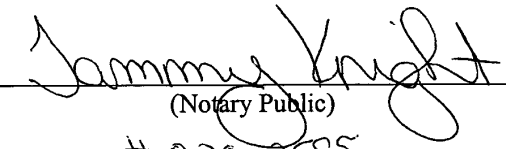
  
Signature

State of Oklahoma     )  
                                  ) ss  
County of Stephens    )

Before me personally appeared said **Trinidad Munoz, Jr.** and acknowledged the foregoing instrument to be his free act and deed this 12<sup>th</sup> day of June, 2003.

Seal

2-13-2006

  
(Notary Public)  
#02002595