

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

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15535 U.S. PTO
60/501049

09/08/03

INVENTOR(S)					
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Kenneth M. Steffan		Ponder Thomas, Jr.		Cumming, Georgia US Buckhead, Georgia US	
<input type="checkbox"/> Additional Inventors are being named on the <u>separately numbered sheets attached hereto.</u>					
TITLE OF THE INVENTION (500 characters max)					
ENVIRONMENTALLY SAFER REPLACEMENT REFRIGERANT WITH NAPHTHENIC OIL FOR REFRIGERANT R22-BASED REFRIGERATION SYSTEMS					
CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number or Bar Code Label		24504 (Insert Customer No. or Attach bar code label here)		or <input type="checkbox"/> Correspondence address below	
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ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages <u>21</u>					
<input type="checkbox"/> CD(s), Number					
<input checked="" type="checkbox"/> Drawing(s) Number of Pages <u>1</u>					
<input type="checkbox"/> Other (Specify)					
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76.					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27				FILING FEE	
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees				AMOUNT (\$)	
<input checked="" type="checkbox"/> The commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number 20-0778				80.00	
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
This invention was made by an agency of the United States government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contact number are:					

Respectfully submitted,

SIGNATURE:

Todd Deveau

Date:

8 Sep. 2003

REGISTRATION NO.: 29,526

TYPE or PRINTED NAME: Todd Deveau

DOCKET NO.: 821920-8010

TELEPHONE: (770) 933-9500

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 USC 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. 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, Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Patent Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

PATENTS
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Kenneth M. Ponder and Steffan Thomas, Jr.

For: Environmentally Safer Replacement Refrigerant With Napthenic Oil for Refrigerant R22-Based Refrigeration Systems

CERTIFICATE OF EXPRESS MAIL
FOR PROVISIONAL APPLICATION

Mail Stop Provisional Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

Enclosed for filing in the above case are the following documents:

Provisional Application Patent Cover Sheet (1 Page)

Provisional Application Consisting of:

21 Page(s) of Specification

1 Page(s) of Drawings (TABLES 3,4)

Fee Transmittal Form

Check for \$80.00

Return Postcard

Further, the Commissioner is authorized to charge Deposit Account No. 20-0778 for any additional fees required. The Commissioner is requested to credit any excess fee paid to Deposit Account No. 20-0778.

Respectfully submitted,



Todd Deveau, Reg. No. 29,526

THOMAS, KAYDEN, HORSTEMEYER
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Our Reference No: **821920-8010**

I hereby certify that all correspondences listed above are being deposited for delivery to the above addressee, with the United States Postal Service **"EXPRESS MAIL POST OFFICE TO ADDRESSEE"** service under 37 CFR §1.10 on the date indicated below.

The envelope has been given U.S. Postal Service "Express Mail Post Office To Addressee" Package # **EL891430145US**.

Date

9/8/07


Laurie Delesandro

15866 U.S. PTO
09/08/03

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.

FEE TRANSMITTAL for FY 2003

Effective 01/01/2003. Patent fees are subject to annual revisions.

☒ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$ **80.00**)

Complete If Known

Application Number	Not Yet Assigned
Filing Date	September 3, 2003
First Named Inventor	Ponder, Kenneth M.
Examiner Name	Not Yet Assigned
Group / Art Unit	Not Yet Assigned
Attorney Docket No.	821920.8010

METHOD OF PAYMENT (check all that apply)

☒ Check ☐ Credit Card ☐ Money Order ☐ Other ☐ None

☒ Deposit Account

Deposit Account Number

20-0778

Deposit Account Name

Thomas, Kayden, Horstemeyer Risley, L.L.P.

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		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1001	750	2001	375	Utility Filing Fee	
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	\$80.00
SUBTOTAL (1)					(\$80.00)

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

		Extra Claims	Fee From Below	Fee Paid
Total Claims		- 20** = 3	X	=
Independent Claims		- 3** = 2	X	=
Multiple Dependent		3		=

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1202	18	2202	9	Claims in excess of 20	3
1201	84	2201	42	Independent claims in excess of 3	2
1203	280	2203	140	Multiple dependent claim, if not paid	3
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)					(\$)

**or number previously paid, if greater; For Reissues, see above

FEES CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
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 ex parte 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 for provisional application	
1806	180	1806	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	750	2809	375	Filing a submission after final rejection (37 CFR § 1.129(a))	
1810	750	2810	375	For each add. 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 exam. of a design application	

Other fee (specify)

SUBTOTAL (3) (\$)

*Reduced by Basic Filing Fee Paid

SUBMITTED BY

Typed or Printed Name
Signature

Todd Deveau

Todd Deveau

Registration No. **29,526**

Telephone Number

770-933-9500

Date

8 Sep. 2003

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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 37 USC 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, Patent and Trademark Office, 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.

EXHIBIT 1015

ENVIRONMENTALLY SAFER REPLACEMENT REFRIGERANT WITH NAPHTHENIC OIL FOR REFRIGERANT R-22-BASED REFRIGERATION SYSTEMS

BACKGROUND OF THE INVENTION

1. Field Of The Invention

The present invention relates to the replacement of Refrigerant R-22 (chlorodifluoromethane) refrigerant with a blend refrigerant that is less damaging to the ozone layer in systems designed to use Refrigerant R-22 (chlorodifluoromethane). More particularly the present invention relates to an improved refrigerant composition, method and apparatus for refrigeration wherein two non-Refrigerant R-22 refrigerants are mixed in a defined ratio such that the temperature-pressure relationship of the mix approximates that of Refrigerant R-22 (chlorodifluoromethane). The mixture is compatible with Refrigerant R-22 (chlorodifluoromethane) so that it can be added to supplement and replace Refrigerant R-22 (chlorodifluoromethane). A further particularity of the instant invention relates to an improved method and apparatus for refrigeration wherein refrigerant mixture is mixed with a soluble lubricating oil to provide lubrication to the apparatus. The lubricant is soluble in both the mixture of the invention and Refrigerant R-22 (chlorodifluoromethane) refrigerant.

2. General Background

Until recently, R-22 refrigerant chlorodifluoromethane (hereinafter sometimes called "Refrigerant R-22 (chlorodifluoromethane)") was the major, if not sole refrigerant, used in residential air-conditioners, refrigerators, freezers and window air-conditioning units. Refrigerant R-22 (chlorodifluoromethane) is a trademark of E. I. du Pont de Nemours & Co. Inc. for chlorodifluoromethane. Hereinafter, "Refrigerant R-22 (chlorodifluoromethane)" is used in this specification to denote chlorodifluoromethane, regardless of the source.

Recently, however, Refrigerant R-22 (chlorodifluoromethane) has come under attack both nationally and internationally as an ozone layer-damaging chemical. In recent years, both the national and international scientific communities have linked Refrigerant R-22 (chlorodifluoromethane) with damage to the earth's protective ozone layer. Air-conditioners,

refrigerator/freezers and window air-conditioning units containing R-22 are believed to be a global source of ozone-damaging material.

In response to scientific concern and a national and global outcry over the use of Refrigerant R-22 (chlorodifluoromethane) in air-conditioning, the United States Congress has acted to first reduce and then ban the use of Refrigerant R-22 (chlorodifluoromethane) in air-conditioning units.

As a first step toward phasing out the use of Refrigerant R-22 (chlorodifluoromethane) in air-conditioning units, Congress is phasing out the use of Refrigerant R-22 (chlorodifluoromethane) in new equipment effective 01/01/2015 and has banned the sale of Refrigerant R-22 (chlorodifluoromethane) in any size container as of 01/01/2020. One of the first areas in which the use of Refrigerant R-22 (chlorodifluoromethane) is to be phased out is in the Bakery industry under the Bakery Partnership Program. Another step in phasing out the use of R-22 is the import restrictions that begin in 2003, limiting the amount of R-22 that can be imported into the United States.

At the time of this application, the vast majority of residential, window units and freezers in use in the United States contain Refrigerant R-22 (chlorodifluoromethane).

Prior to banning the sale of quantities of Refrigerant R-22 (chlorodifluoromethane), owners of equipment with Refrigerant R-22 (chlorodifluoromethane)-based air-conditioning units are able to purchase the level of refrigerant in their equipment with only the need of a refrigerants license as required by the Clean Air Act. Millions of units containing refrigerant R-22 (chlorodifluoromethane) were sold in the United States prior to the start of mandatory phase out set forth by Congress and the international community.

Refrigerant R-22 (chlorodifluoromethane) recharging typically involves 30 lb. cans or cylinders typically used in the HVAC/R industry. The cylinders are fitted with a dispensing outlet compatible with a commercially available refrigeration manifold. In order to recharge an air-conditioning system, a customer need to only fit the can or cylinder to the manifold and discharge, or "add to" the refrigerant charge directly into the air conditioning system.

Following Congress's ban on the sale of Refrigerant R-22 (chlorodifluoromethane) millions of equipment owners with Refrigerant R-22 (chlorodifluoromethane)-based air-conditioning units will be left with no choice other than to seek replacement refrigerants to service these units. Intentionally mixing of refrigerants is currently illegal by standards set forth by the Clean Air Act. An example would be for this application is that current R-22 units could not be mixed with this invention intentionally.

In response to Congress's ban on the use of Refrigerant R-22 (chlorodifluoromethane) in air-conditioning, service dealers have begun to retrofit existing Refrigerant R-22 (chlorodifluoromethane)-based air-conditioning units with new, non-R-22 refrigerants, such as R410A (a 50/50 mixture of difluoromethane and pentafluoroethane), R417 (a 46/50/4 mixture of pentafluoroethane, 1,1,1,2-tetrafluoroethane, and butane) or R407C (a 23/25/52 mixture of difluoromethane, pentafluoroethane, and 1,1,1,2-tetrafluoroethane). None of these replacements contain a lubricant when produced.

The refrigerants that will be authorized by the Environmental Protection Agency (EPA) to replace Refrigerant R-22 (chlorodifluoromethane) in air conditioners is currently under review and will evolve to require an environmentally safe refrigerant, with a 0 odp factor like the one of the present invention described herein. Unfortunately, most replacements for R-22 have a markedly different temperature-pressure relationship at most operating temperatures than Refrigerant R-22 (chlorodifluoromethane).

Because of this difference in the temperature-pressure relationship of Refrigerant R-22 (chlorodifluoromethane) and current replacement refrigerants, existing Refrigerant R-22 (chlorodifluoromethane)-based systems cannot typically be interchanged. Hence, non-retrofitted, Refrigerant R-22 (chlorodifluoromethane)-based units have a need for a refrigerant that will fulfill the requirements of the system design while also meeting the requirements of the EPA and the international community.

Simply mixing refrigerants with existing Refrigerant R-22 (chlorodifluoromethane) in order to replenish, or "toping off" the level is against the law and not feasible. When other refrigerants are mixed with Refrigerant R-22 (chlorodifluoromethane), the mixture can take on the pressure characteristics of a substance that could be harmful to either the equipment or the

operator. The temperature-pressure relationship becomes markedly different from that of Refrigerant R-22 (chlorodifluoromethane) at temperatures within the normal refrigerant operating temperature range and typical use of R-22.

Hence, in the absence of Refrigerant R-22 (chlorodifluoromethane) owners of equipment with Refrigerant R-22 (chlorodifluoromethane)-based air conditioners face but one choice when the level of their air-conditioning coolant is low: professional service—at a significant cost—to remove the existing Refrigerant R-22 (chlorodifluoromethane), and retrofit the system compatible with some kind of refrigerant gas.

R-22 refrigerants were developed to replace the prior, now banned R-12 refrigerant, or dichlorodifluoromethane. R-12 is sometimes referred to as FREON 12®, which is a trademark of E.I. du Pont de Nemours & Co. for dichlorodifluoromethane.

Thomas et al. (U.S. Pat. No. 5,254,280) discloses a lubricant developed for use with a refrigerant known as R134a (1,1,1,2 – tetrafluoroethane) and the combination of that lubricant with a refrigerant, which is a replacement for R-12. The lubricant contains polyoxyalkylene glycol, which is hydrophilic and could damage the system as discussed below.

Wilczek (U.S. Pat. No. 5,384,057), Gorski (U.S. Pat. No. 4,971,712), and Anton of DuPont (U.S. Pat. No. 5,145,594) disclose other R-12 replacements in the form of a blend of certain synthetic lubricants in various R134a and R134a/R125 refrigerant systems. The DuPont patents discuss a gas known as R125 (pentafluoroethane). R125 is five fluorine atoms bonded to an ethane molecule. This is a very large molecule for a refrigerant. It is currently being produced for refrigeration only. Anton discloses the use of a lubricant comprising at least one cyanocarbon compound. Wilczek discloses a fluorosiloxane as a lubricant. Gorski discloses a polyalkylene glycol as a lubricant.

Systems that contain R-22, or R-12 replacements, are still being produced today. These older systems have common components: R-22, R-22 mineral oil lubricant, and water that is sequestered into the dryer. If R134a (1,1,1,2-tetrafluoroethane) were added to the system, it would damage the system as follows: (1) if no lubricant is added to the R134a (as in U.S. Pat. No. 4,953,312 to Tamura et al.), then the R-22 system would be starved for lubricant, since the

R134a gas is not miscible with the mineral oil lubricant; (2) if a synthetic lubricant is added to the R134a (as in Thomas et al.), then there is a different problem—that of moisture. Older systems can have water trapped in their dryers. The synthetic lubricants (such as polyglycol- or polysiloxane-based lubricants) are hydrophilic. Thus, they are not only miscible with R-22 and R134a; they are also partially or completely miscible with water. Thus, if they are introduced into an R-22 system, they will pull this water out of the dryer into the refrigerant flow, initiating corrosion and damage to pressure switches and the TX valve and possible other system components. This is why Elf Atochem and DuPont, to name a few publish elaborate flushing procedures and high efficiency dryer change-outs to prevent damage to the cooling system.

Weber (U.S. Patent No. 5,942,149) discloses yet another R-12 replacement consisting of a blend of chlorodifluoroethane, tetrafluoroethane and a napthenic lubricating oil.

SUMMARY OF THE PRESENT INVENTION

The invention provides a method and apparatus that are environmentally sound alternatives to the use of Refrigerant R-22 (chlorodifluoromethane) as a refrigerant. More particularly, the invention provides a mixture of at least two refrigerants that are miscible with each other, and compatible with Refrigerant R-22 (chlorodifluoromethane) while at the same time possessing a temperature-pressure profile that approximates that of Refrigerant R-22 (chlorodifluoromethane) over the operating range of ambient temperatures usually encountered by air conditioning units or other apparatus utilizing Refrigerant R-22 (chlorodifluoromethane) as a refrigerant. The invention also provides a lubricant, that is compatible with both the environmentally sound refrigerant of the invention and with Refrigerant R-22 (chlorodifluoromethane), so that mixtures of the refrigerant according to the invention and Refrigerant R-22 (chlorodifluoromethane) may be utilized with this lubricant in the refrigeration systems without deleterious effect upon moving parts of the refrigerating apparatus that require lubrication from the refrigerant.

More particularly, the invention provides a mixture of pentafluoroethane and tetrafluoroethane in specific proportions that provide a temperature-pressure relationship that approximates that of Refrigerant R-22 (chlorodifluoromethane) over the range of ambient temperature operating conditions in which Refrigerant R-22 (chlorodifluoromethane) is a useful

refrigerant. The tetrafluoroethane can be either 1,1,1,2-tetrafluoroethane or 1,1,2,2-tetrafluoroethane. In an exemplary embodiment, the refrigerant according to the invention comprises a ratio of from about 40 to about 45 weight percent pentafluoroethane to about 55 to about 60 percent 1,1,1,2-tetrafluoroethane, based upon the total weight of pentafluoroethane and 1,1,1,2-tetrafluoroethane. In a further exemplary embodiment, the refrigerant includes the ratio of about 42 weight percent pentafluoroethane to about 58 weight percent 1,1,1,2-tetrafluoroethane. In addition, the refrigerant according to the invention also includes from about 0.5 to about 2 weight percent (based on the combined weight of pentafluoroethane and 1,1,1,2-tetrafluoroethane) of a napthenic or paraffinic based lubricating oil that is soluble in chlorodifluoromethane, pentafluoroethane, and 1,1,1,2-tetrafluoroethane. In an exemplary embodiment, the lubricant is selected from those lubricants sold by Anderol, Inc., East Hanover, N.J., an affiliate of Royal Lubricants Company, under the trademark ROYCO® 2302. It should be understood, however, that other lubricating oils might also be used, as long as they are compatible with pentafluoroethane, 1,1,1,2-tetrafluoroethane, and Refrigerant R-22 (chlorodifluoromethane).

ROYCO® 2302 is a napthenic oil lubricant having the following composition:

65-85% hydrotreated light napthenic distillate,
10-20% solvent refined light napthenic distillate petroleum,
<0.5% butylated triphenyl phosphate, and
<2% minor additive.

While it is intended that the substitute refrigerant according to the invention may be utilized to replace Refrigerant R-22 (chlorodifluoromethane) that has escaped from an apparatus, the substitute refrigerant of the invention may also be utilized to completely refill apparatus that have been designed for use with Refrigerant R-22 (chlorodifluoromethane), since the refrigerant has a temperature-pressure profile that closely approximates that of Refrigerant R-22 (chlorodifluoromethane). Thus, when the refrigerant is used as a complete replacement for Refrigerant R-22 (chlorodifluoromethane), it is no longer necessary that the lubricant be compatible with chlorodifluoromethane but only that it should be compatible with 1,1,1,2-tetrafluoroethane and pentafluoroethane.

Further, whereas the substitute refrigerant of the invention is less damaging to the ozone layer than Refrigerant R-22 (chlorodifluoromethane) and is useful in air conditioning units, and in particular residential type air-conditioning units, it is not so limited in its use. Indeed, the refrigerant may be utilized as a substitute or replacement for Refrigerant R-22 (chlorodifluoromethane) in virtually any application, thereby eliminating the use of ozone layer-damaging Refrigerant R-22 (chlorodifluoromethane).

In further specifics, the invention provides a canister containing a mixture of tetrafluoroethane and pentafluoroethane with a napthenic oil that may be fitted with an outlet manifold that is compatible with a Refrigerant R-22 (chlorodifluoromethane) recharging manifold that is typically used to recharge an apparatus with the latter refrigerant. Refrigerant may then be allowed to flow from the container through the manifold and into the apparatus to replace Refrigerant R-22 (chlorodifluoromethane) refrigerant that has been lost from the refrigeration system.

When mixing the components of the refrigerant blend of the present invention, one should first mix the lubricant with the tetrafluoroethane, then mix that mixture with the pentafluoroethane in the proportions afore mentioned. Otherwise, the product does not mix properly.

In an exemplary form, the lubricant has a viscosity of 5 to 500 centistokes, more preferably 5 to 100 centistokes, even more preferably 5 to 50 centistokes, and most preferably 5 to 10 centistokes. The lubricant having a viscosity of 5 to 10 centistokes is preferred.

In an exemplary embodiment, the percentage by weight of lubricant in the refrigerant blend is 0.5-2%, more preferably 1-2%, even more preferably 1.25-2%, and most preferably 1.5-1.75%. The percentage by weight of lubricant in the refrigerant blend is, for example, 1.75. \pm .005%.

A suitable lubricant is severely hydro treated napthenic/paraffinic lubricant, such as the aforementioned ROYCO® 2302. Other suitable lubricants include Sunpar R2280 (a paraffinic based lubricant), Lubrizol 403, and Sunthene 200 (a napthenic based lubricant). Mobil One 5-

weight naphthenic paraffinic synthetic oil (it is hydrophobic) could also work as a lubricant, but it is relatively expensive.

A corrosion inhibitor can be included. (otherwise corrosion will probably occur within 6 months). An exemplary corrosion inhibitor is one for anhydrous systems (such corrosion inhibitors comprise calcium, or phosphate salts). The corrosion inhibitor can be bonded to the lubricant.

The lubricant is preferably hydrophobic (immiscible with water). Preferably no more than 5% by weight of the lubricant is hydrophilic lubricant (some aliphatic hydrocarbon solvents can absorb up to 5% by weight water and still maintain lubricating integrity). More preferably, no more than 2% by weight of the lubricant is hydrophilic lubricant. Most preferably, the refrigerant blend contains no hydrophilic lubricant.

In order for the parts of the refrigerant system to function properly, 0.5-2% of total weight of refrigerant should be lubricant. When adding the refrigerant blend to a refrigerant system, one should leave the lubricant in the system if one for some reason takes out the Refrigerant R-22.

The present invention is designed to be utilized as a R-22 replacement in refrigeration systems. It is designed as a replacement, in which little or no modifications including parts are used to adapt the system for the refrigerant of the present invention.

The naphthenic, mineral oil based lubricant system of the claimed invention is miscible with the pentafluoroethane and tetrafluoroethane blend and with R-22 refrigerant. This allows for mixing of residual R-22 refrigerant and the refrigerant of the present invention, without the release of residual water in the dryer and subsequent system damage (as will happen if the synthetic lubricants disclosed in Thomas et al. and the DuPont patents are used).

The present invention can be used as a replacement for R-22 refrigerant, typically deminus without retrofitting the air conditioning system or flushing it out. It is recommended that a full vacuum be obtained before adding the refrigerant to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention provides a mixture of non-Refrigerant 22 refrigerants that are less damaging to the Earth's ozone layer and that are approved by the U.S. Environmental Protection Agency for use in air-conditioners. The invention mixture is compatible with Refrigerant R-22 (chlorodifluoromethane) and can be used to replace existing Refrigerant R-22 (chlorodifluoromethane)-in R-22 based refrigeration systems. It is expected that the present invention will gradually replace Refrigerant R-22 (chlorodifluoromethane) in Refrigerant R-22 (chlorodifluoromethane)-based air-cooling systems, without the need to retrofit existing Refrigerant R-22 (chlorodifluoromethane)-based systems for non-Refrigerant 22 replacement refrigerants.

Specifically, the present invention includes a mixture of pentafluoroethane and tetrafluoroethane and a compatible naphthenic or paraffinic based lubricant, such as ROYCO® 2302, provided under pressure in a can or cylinder equipped with an outlet compatible with existing Refrigerant R-22 (chlorodifluoromethane) recharging kit manifolds, so that the refrigerant and lubricant mixture can be added to existing Refrigerant R-22 (chlorodifluoromethane) based coolant systems. Also, the invention provides the possibility of using new refrigerant systems, originally designed for "Refrigerant R-22 (chlorodifluoromethane)," by supplying an EPA-approved refrigerant so that retrofitting to new equipment use is not required.

In an exemplary embodiment, the invention provides an cylinder can like the standard 25 or 30 lb. can formerly used for containing "Refrigerant R-22 (chlorodifluoromethane)," but containing about 58% by weight 1,1,1,2-tetrafluoroethane and about 42% by weight pentafluoroethane. The can also contains the preferred lubricant, ROYCO® 2302 in solution with the coolant mixture at a percent by weight of between 0.5% and 2%.

Existing Refrigerant R-22 (chlorodifluoromethane)-based air-conditioning systems use an amount of a vegetable or hydrocarbon mineral oil to lubricate the compressor. This oil has a very low vapor pressure, and is not soluble with pure tetrafluoroethane, particularly 1,1,1,2-tetrafluoroethane. Hence, adding tetrafluoroethane to replace Refrigerant R-22 (chlorodifluoromethane) in existing Refrigerant R-22 (chlorodifluoromethane)-based air-

conditioning systems leads to compressor breakdown from lack of sufficient lubrication. The invention provides lubricants that are compatible with the invention mixture of tetrafluoroethane and pentafluoroethane, and with "Refrigerant R-22 (chlorodifluoromethane)," and that are suitable for lubricating refrigerant compressors and other air-conditioner component parts. The most preferred ROYCO® 2302 lubricants, on the other hand, are soluble in a tetrafluoroethane/pentafluoroethane mixture. This solubility allows the replacement refrigerant blend to lubricate the air-conditioning system, preventing damage to the compressor and component parts of the system.

EXAMPLE 1

Table 1 summarizes the results of solubility tests of a 2% by weight solution of ROYCO® 2302 oil lubricant in an 58/42% by weight mixture of 1,1,1,2-tetrafluoroethane and pentafluoroethane refrigerants. ROYCO® 2302 oil (available from ANDEROL®, Inc., an affiliate of Royal Lubricants Co.), was added to a clear Fisher-Porter pressure burette and a mixture of 1,1,1,2-tetrafluoroethane/pentafluoroethane in an 58/42 ratio by weight was introduced under pressure to maintain the liquid state.

TABLE 1

Full Burette	clear no separation
2/3 Full Burette	clear no separation
1/2 Full Burette	clear no separation
1/3 Full Burette	clear no separation
Almost Empty Burette	clear no separation

Note: The color of the fluid remained the same as the burette was emptied. The expelled gas deposited the oil onto a test panel.

EXAMPLE 2

In the invention, 1,1,1,2-tetrafluoroethane and pentafluoroethane are mixed with the napthenic oil lubricant at set ratios such that the temperature-pressure profile of the mixture is similar to that of Refrigerant R-22 (chlorodifluoromethane), over the normal operating range of air-conditioners. Table 2 summarizes the results of tests of the temperature-pressure profiles of

various mixes of 1,1,1,2-tetrafluoroethane and pentafluoroethane over the range of normal air-conditioner working temperatures, from -60 degree. F. to 160. degree. F.

For Table 2, different percentages of 1,1,1,2-tetrafluoroethane and pentafluoroethane --by weight--were mixed with the lubricant to show the pressure temperature relationships of the various invention combinations.

Table 3 shows P (liquid) vs. Temperature

Table 4 shows Temperature vs. Enthalpy

This invention shows the following points of interest concerning this blend for the

Dew Point @ -32F

Bubble Point @ -41.5F

Glide @ 9.5 F

The most preferred ratio is about 42% by weight pentafluoroethane and about 58% by weight 1,1,1,2-tetrafluoroethane. This is the ratio of pentafluoroethane to 1,1,1,2-tetrafluoroethane with the lubricant where the mixture of the invention shows the greatest similarity to "Refrigerant R-22 (chlorodifluoromethane)", over most operating temperatures.

In the most preferred embodiment of the composition, the most preferred ratios of 1,1,1,2-tetrafluoroethane and pentafluoroethane are mixed with a range of from 0.5% to 2% by weight of ROYCO® 2302 lubricant or similar type napthenic oil lubricant as aforementioned.

The apparatus and method of the preferred embodiment encompass the use of a mixture of 1,1,1,2-tetrafluoroethane and pentafluoroethane at preferred ranges, as discussed above, with ROYCO® 2302 lubricant at preferred ranges, as discussed above (0.5-2% by weight) in the operation of an air-conditioning system, wherein the coolant-oil mixture replaces Refrigerant R-22 (chlorodifluoromethane) in a Refrigerant R-22 (chlorodifluoromethane)-based refrigeration system.

The method and apparatus in the preferred embodiment further details providing the above described mix of pentafluoroethane/1,1,1,2-tetrafluoroethane and ROYCO® 2302 in 30 lb

cylinders, where the cylinders are pressure sealed and fitted with an outlet compatible for existing Refrigerant 22-type refrigeration manifolds typically ¼ inch male flare.

Further, it was noted that the systems tested ran more smoothly and the compressor showed less vibration during the test period, as the mixture of the invention was added. It is theorized that the lubricating oil, being soluble in the refrigerant gasses, was better able to lubricate the compressor and reciprocating parts than the existing Refrigerant R-22 (chlorodifluoromethane) lubricant used by itself. In some applications a reduction in power consumption maybe also noted.

The refrigerant of the present invention can also be used as a replacement refrigerant for the new R-22 air-conditioning systems, such as the systems used in today's HFC-free units

The lubricant of the present invention preferably has a flash point of more than 150 degrees F. Pure refrigerant 1,1,1,2-tetrafluoroethane is not miscible with a napthenic lubricant like mineral oil or mineral seal oil (both of which could be used as the lubricants of the present invention). Pentafluoroethane is miscible with most napthenic lubricants, including mineral oils. The presence of the pentafluoroethane allows the use of mineral oils in the refrigerant blend and system of the present invention (a translucent, partially miscible blend is formed). The lubricant can advantageously be partially polymerized into longer chain molecules to allow it to function at very low percentage levels. The lubricant can be hydrotreated or polymerized for stability and wear resistance.

Phosphated additives add corrosion resistance in the presence of acids and salts and increase wear resistance. Calcium additives help the lubricant resist rust and the effects of corrosion; calcium salts reduce the corrosive effects of hydrochloric acid that is formed in the presence of water and the chlorinated gases present in the refrigerant systems of the present invention.

The ROYCO® lubricants mentioned above contain the corrosion inhibitors mentioned above and also contain acrylic polymer. It is believed that the function of the acrylic polymer is to increase wear resistance under severe conditions. Acrylics can help film formation, and the ability of the lubricant to coat metal and soft parts and stay in place.

The lubricant of the present invention is miscible with R-22, the R-22 lubricant, and the blend of the refrigerant gases of the present invention.

It should be understood that variations and modifications may be made of the invention herein taught, and that those are within the scope and spirit of the invention as taught above and claimed here below.

Table 2

Temp (F)	P (60-40)	P (58-42)	P (55-45)	P (R-22)
-60	8.982	8.81	8.552	8.836
-55	10.36	10.16	9.87	10.19
-50	11.9	11.68	11.35	11.7
-45	13.62	13.37	12.99	13.39
-40	15.52	15.24	14.82	15.26
-35	17.63	17.32	16.84	17.34
-30	19.96	19.61	19.08	19.62
-25	22.52	22.13	21.54	22.14
-20	25.33	24.9	24.25	24.91
-15	28.41	27.93	27.21	27.93
-10	31.76	31.23	30.44	31.23
-5	35.42	34.83	33.96	34.82
0	39.39	38.74	37.79	38.73
5	43.69	42.98	41.94	42.96
10	48.34	47.57	46.43	47.54
15	53.36	52.52	51.27	52.48
20	58.76	57.85	56.5	57.79
25	64.57	63.58	62.11	63.51
30	70.8	69.73	68.14	69.65
35	77.48	76.33	74.61	76.22
40	84.62	83.38	81.52	83.26
45	92.25	90.9	88.91	90.76
50	100.4	98.93	96.79	98.76
55	109	107.5	105.2	107.3
60	118.2	116.6	114.1	116.3
65	128	126.2	123.6	125.9
70	138.4	136.5	133.6	136.1
75	149.3	147.3	144.3	146.9
80	160.9	158.8	155.6	158.3
85	173.2	170.9	167.5	170.4
90	186.1	183.7	180.1	183.1
95	199.8	197.2	193.3	196.5
100	214.2	211.4	207.3	210.6
105	229.3	226.4	222.1	225.5
110	245.3	242.2	237.6	241.1
115	262	258.7	253.9	257.5
120	279.6	276.1	271	274.7
125	298.1	294.4	289	292.7
130	317.5	313.6	307.8	311.6
135	337.8	333.7	327.6	331.4
140	359.1	354.8	348.3	352.1
145	381.4	376.8	370.1	373.7
150	404.8	400	392.8	396.4
155	429.3	424.2	416.7	420
160	454.9	449.5	441.6	444.7

Claims

What is claimed as invention is:

1. In an apparatus for refrigerating that is designed for use with ozone layer-damaging chlorodifluoromethane refrigerant known as R-22, the improvement comprising substituting the chlorodifluoromethane with a substitute blend refrigerant containing a napthenic lubricant less damaging to the Earth's ozone layer than chlorodifluoromethane,

said substitute refrigerant consisting of:

about 40% to about 45% by weight pentafluoroethane;

about 55% to about 60% by weight tetrafluoroethane; and

packaged with about 0.5% to about 2% by weight of the refrigerant with napthenic or paraffinic based lubricating oil that is soluble in chlorodifluoromethane, pentafluoroethane and tetrafluoroethane.

2. The invention according to Claim 1, the napthenic lubricating oil having the following components:

65-88% hydrotreated light napthenic distillate, and

10-20% solvent refined light napthenic distillate petroleum.

3. The invention according to claim 1 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 40% by weight to said tetrafluoroethane present in an amount of about 60% by weight.

4. The invention according to claim 1 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 42% by weight to said tetrafluoroethane present in an amount of about 58% by weight.

5. The invention according to claim 1 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 45% by weight to said tetrafluoroethane present in an amount of about 55% by weight.

6. A method for refilling an apparatus for refrigeration that is designed for use with ozone layer-damaging chlorodifluoromethane refrigerant, the method comprising:

(1) supplying a substitute refrigerant under pressure, in a cylinder can fitted with an outlet compatible with a chlorodifluoromethane recharging manifold of the apparatus; and

(2) adding to said apparatus via the manifold a substitute refrigerant for chlorodifluoromethane, wherein said substitute refrigerant consists of:

about 40% to about 45% by weight pentafluoroethane ;

about 55% to about 60% by weight tetrafluoroethane; and

about 0.5% to about 2% by weight of the refrigerant of a lubricating oil that is soluble in chlorodifluoromethane, pentafluoroethane and tetrafluoroethane.

7. The invention according to claim 6, the lubricating oil having the following components:

65-85% hydrotreated light napthenic distillate, and

10-20% solvent refined light napthenic distillate petroleum.

8. The invention according to claim 6 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 40% by weight to said tetrafluoroethane present in an amount of about 60% by weight.

9. The invention according to claim 6 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 42% by weight to said tetrafluoroethane present in an amount of about 58% by weight.

10. The invention according to claim 6 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 45% by weight to said tetrafluoroethane present in an amount of about 55% by weight.

11. In an apparatus for air-conditioning designed for use with ozone layer-damaging chlorodifluoromethane refrigerant the improvement comprising substituting the chlorodifluoromethane with a refrigerant less damaging to the Earth's ozone layer than chlorodifluoromethane, the substitute refrigerant consisting of:

about 40% to about 45% by weight pentafluoroethane;

about 55% to about 60% by weight tetrafluoroethane; and

about 0.5% to about 2% by weight of the refrigerant of a lubricating oil that is soluble in chlorodifluoromethane, pentafluoroethane and tetrafluoroethane.

12. The invention according to claim 11, the lubricating oil having the following components:

65-85% hydrotreated light napthenic distillate, and

10-20% solvent refined light napthenic distillate petroleum.

13. The invention according to claim 11 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 42% by weight to said tetrafluoroethane present in an amount of about 58% by weight.

14. The invention according to claim 11 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 45% by weight to said tetrafluoroethane present in an amount of about 55% by weight.

15. The invention according to claim 11 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 40% by weight to said tetrafluoroethane present in an amount of about 60% by weight.

16. A method for refilling an apparatus for air-conditioning that is designed for use with ozone layer-damaging chlorodifluoromethane refrigerant, the method comprising:

(1) supplying a substitute refrigerant under pressure in a cylinder can fitted with an outlet compatible with a chlorodifluoromethane recharging manifold of the apparatus; and

(2) adding to said apparatus via the manifold the substitute refrigerant for chlorodifluoromethane, wherein said substitute refrigerant consists of:

about 40% to about 45% by weight pentafluoroethane ;

about 55% to about 60% by weight tetrafluoroethane; and

about 0.5% to about 2% by weight of the refrigerant of a lubricating oil that is soluble in chlorodifluoromethane, pentafluoroethane and tetrafluoroethane.

17. The invention according to claim 16, the lubricating oil having the following components:

65-85% hydrotreated light napthenic distillate, and

10-20% solvent refined light napthenic distillate petroleum.

18. The invention according to claim 16 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 42% by weight to said tetrafluoroethane present in an amount of about 58% by weight.

19. The invention according to claim 16 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 45% by weight to said tetrafluoroethane present in an amount of about 55% by weight.

20. The invention according to claim 16 wherein in the substitute refrigerant said pentafluoroethane is present in the ratio of about 40% by weight to said tetrafluoroethane present in an amount of about 60% by weight.

21. A refrigerant consisting of:

about 40% to about 45% by weight pentafluoroethane;

about 55% to about 60% by weight tetrafluoroethane; and

about 0.5% to about 2% by weight of the refrigerant of a lubricating oil that is soluble in chlorodifluoromethane, pentafluoroethane and tetrafluoroethane.

22. The invention according to claim 21, the lubricating oil having the following components:

65-85% hydrotreated light napthenic distillate, and

10-20% solvent refined light napthenic distillate petroleum.

23. A refrigerant according to claim 21 wherein said pentafluoroethane is present in the ratio of about 40% by weight to said tetrafluoroethane present in an amount of about 60% by weight.

24. A refrigerant according to claim 21 wherein said pentafluoroethane is present in the ratio of about 45% by weight to said tetrafluoroethane present in an amount of about 55% by weight with a napthenic lubricant.

25. A refrigerant according to claim 21 wherein said pentafluoroethane is present in the ratio of about 40% by weight to said tetrafluoroethane present in an amount of about 60% by weight with a napthenic lubricant.

26. The invention according to any one of claims 1, 6, 11, 16, and 21, wherein the tetrafluoroethane is 1,1,1,2-tetrafluoroethane.

27. The invention according to any one of claims 2, 7, 12, 17, and 22, wherein the lubricating oil further includes an acrylic polymer.

28. The invention according to any one of claims 2, 7, 12, 17, and 22, wherein the lubricating oil further includes a corrosion inhibitor.

29. The invention according to any one of claims 6, 11, 16, and 21, wherein the lubricating oil is selected from the group consisting of napthenic based lubricants, paraffinic based lubricants and mixtures thereof.

ABSTRACT

An apparatus and method wherein potential ozone layer-damaging chlorodifluoromethane (Refrigerant R-22) is substituted with a mix of less environmentally damaging refrigerants Pentafluoroethane and Tetrafluoroethane in chlorodifluoromethane-based air-cooling systems mainly in residential cooling. While less environmentally damaging than chlorodifluoromethane, the substitute refrigerant has a temperature-pressure relationship similar to that of chlorodifluoromethane, making the substitute refrigerant suitable for use with chlorodifluoromethane-based air-cooling systems. In this event, it is mixed with a relatively small percentage of a napthenic lubricating oil which is compatible with both the unit refrigerant and typical R-22 system design.

Table 3

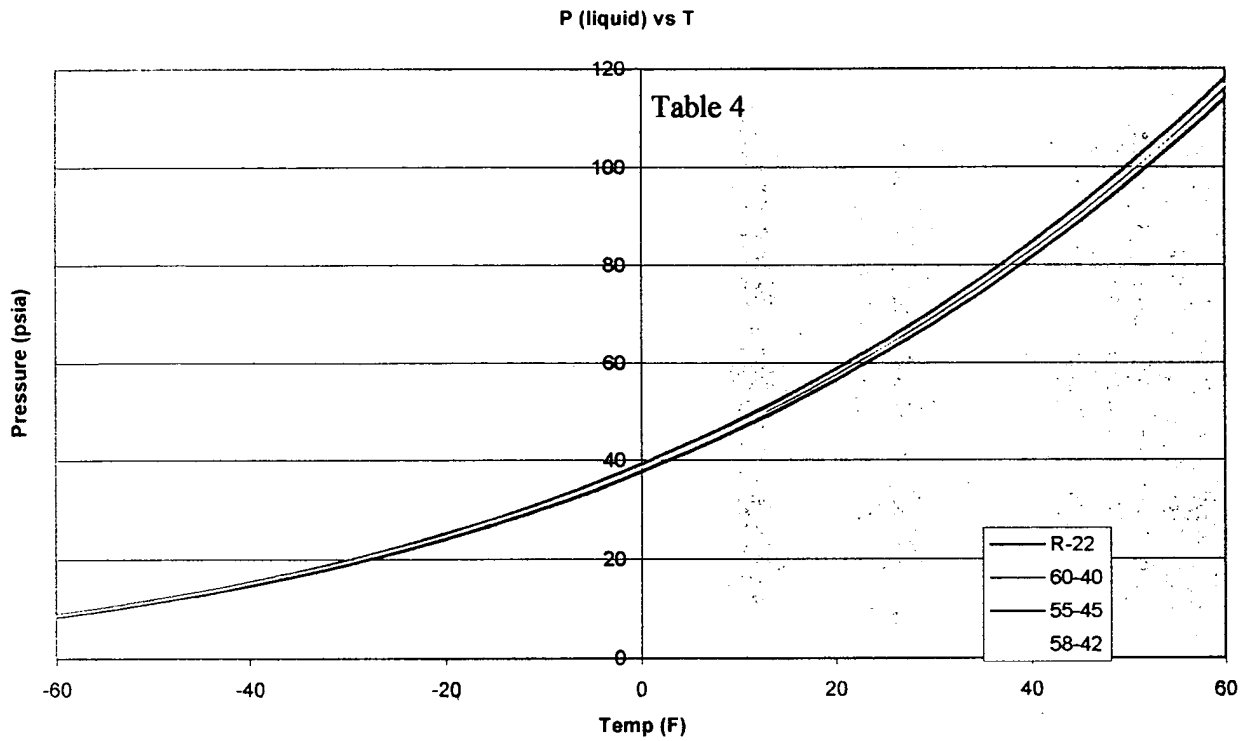
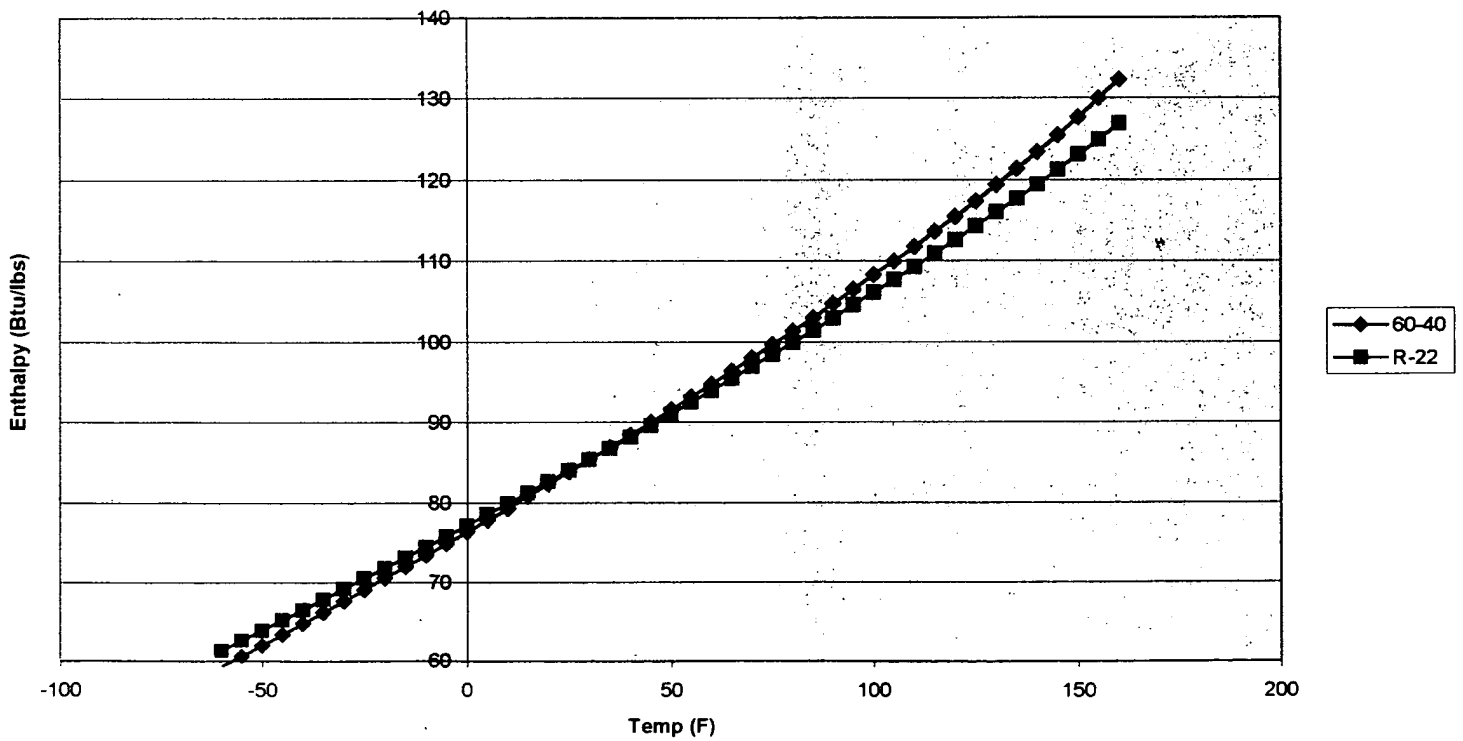


Table 4
Temp vs Enthalpy



PATENT APPLICATION SERIAL NO. _____

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE
FEE RECORD SHEET

09/10/2003 SHINASS1 00000093 60501049

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Doc Code: Computer

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Stapled Set(s) of Extra Color Drawings/Photographs

Doc Code: Artifact Artifact Type Code: C

☐

CD(s) containing pages of specification ☐
and/or sequence listing ☐

Doc Code: Artifact

Artifact Type Code: S

☐

CD(s) with content unspecified

Doc Code: Artifact Artifact Type Code: U

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Microfilm(s)

Doc Code: Artifact Artifact Type Code: F

☐

Video tape(s)

Doc Code: Artifact Artifact Type Code: V

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Model(s)

Doc Code: Artifact Artifact Type Code: M

☐

Bound Document(s)

Doc Code: Artifact Artifact Type Code: B

☐

Other, description: _____

Doc Code: Artifact

Artifact Type Code: Z