

(19) Japan Patent Office (JP)
(12) Official Gazette for Unexamined Patent Publications (A)
(11) Patent Application Publication No.: S59-70626
5
(51) Int.Cl.³
C 07 C 21/21
17/34

10 Identification Symbol

Intra-Agency Serial Number
8217-4H
8217-4H

15
(43) Publication Date: April 21, Showa Year 59 (1984)
Number of Inventions: 1
Request for Examination: Not Requested
(Total of 7 Pages [in the Japanese text])

20
(54) A method for the production of chloroprene
(21) Patent Application No.: S57-182624
(22) Filing Date: October 18, Showa Year 57 (1982)
(72) Inventor: Sasayama Masayuki
25 No. 2209 Oumi-Cho Oaza Oumi, Nishikubiki County,
Niigata Prefecture - Denki Kagaku Kogyo Co., Ltd. Oumi
Plant
(72) Inventor: Tabata Itsuo
No. 2209 Oumi-Cho Oaza Oumi, Nishikubiki County,
30 Niigata Prefecture - Denki Kagaku Kogyo Co., Ltd. Oumi
Plant
(72) Inventor: Yagi Yuji
No. 2209 Oumi-Cho Oaza Oumi, Nishikubiki County,
Niigata Prefecture - Denki Kagaku Kogyo Co., Ltd. Oumi
35 Plant
(72) Inventor: Utagawa Masao
No. 2209 Oumi-Cho Oaza Oumi, Nishikubiki County,
Niigata Prefecture - Denki Kagaku Kogyo Co., Ltd. Oumi
Plant

(71) Patent Applicant: Denki Kagaku Kogyo Co., Ltd.

4-1 1-Chome, Yuraku-Cho, Chiyoda Ward, Tokyo

Specification

5

1. Name of the Invention

A method for the production of chloroprene

2. Scope of the Patent Claims

10 1. A method for the production of chloroprene which is characterized in that chloroprene is produced by subjecting 3,4-dichloro-butene-1 to dehydrochlorination in an aqueous solution containing 25 - 55% by weight of an alkali metal hydroxide in the presence of an organic
15 catalyst, wherein a mixture containing chloroprene, unreacted 3,4-dichloro-butene-1 and water produced by performing a reaction at a temperature of 20 - 100°C is removed in a gas phase via evaporation without reflux of said mixture into the reaction system, after which
20 said evaporated mixture is completely condensed, said condensed mixture is separated into an aqueous phase and an organic phase, after which said organic phase is subjected to fractional distillation to separate 3,4-dichloro-butene-1 and chloroprene; and wherein some
25 water is evaporated away at 95 - 100°C from the water phase primarily containing an aqueous solution of alkali metal hydroxide and alkali metal chloride, which in turn contains solid alkali metal chloride left over following removal of the reaction mixture in the gas
30 phase via evaporation, and the resulting material is concentrated to recover an aqueous solution containing alkali metal hydroxide at a concentration of 15 - 55% by weight which is re-used in the reaction.

35 2. A method for the production of chloroprene as specified in Claim 1 which is characterized in that, upon fractional distillation of the organic phase, moisture is removed from said organic phase until moisture content is 0.04% by weight, after which the

organic phase is subject to fractional distillation to separate 3,4-dichloro-butene-1 and chloroprene.

3. A method for the production of chloroprene as specified in Claim 1 which is characterized in that
5 some water is evaporated from the water phase containing primarily an aqueous solution of alkali metal hydroxide and alkali metal chloride, which in turn contains solid alkali metal chloride, and the resulting material is concentrated using a forced
10 circulation concentration apparatus to recover alkali metal hydroxide which is reused in the reaction.

4. A method for the production of chloroprene as specified in Claim 1 or Claim 3 which is characterized in that once the organic phase is separated from the
15 aqueous phase containing primarily an aqueous solution of alkali metal hydroxide and alkali metal chloride, which in turn contains solid alkali metal chloride, some water is evaporated and condensed.

5. A method for the production of chloroprene as specified in Claim 1 which is characterized in that
20 recovered 3,4-dichloro-butene-1 is fed back into the dehydrochlorination reaction for reuse.

6. A method for the production of chloroprene as specified in Claims 1, 3 or 4 which is characterized in
25 that solid alkali metal chloride is separated from an aqueous solution containing primarily alkali metal hydroxide and alkali metal chloride, which contains solid alkali metal chloride, obtained following evaporation of part of the water component and
30 concentration of the resulting material, after which a recovered aqueous solution composed primarily of alkali metal hydroxide and alkali metal chloride is fed back into the dehydrochlorination reaction for reuse.

7. A method for the production of chloroprene as
35 specified in Claim 1 in which a quaternary ammonium compound, quaternary phosphonium compound, sulfonium compound or mixture thereof is used as a reaction catalyst.

3. Detailed Description of the Invention

The present invention relates to an improved process for the production of chloroprene (2-chloro-butadiene-1,3), via the dehydrochlorination of 3,4-dichloro-butene-1.

Methods for the production of chloroprene via the dehydrochlorination of 3,4-dichloro-butene-1 which employ an alkaline aqueous solution are already known. However, conventional methods have the disadvantage of slow reaction rates as well as significant production of undesirable byproducts such as 1-chloro-butadiene-1,3, so a method for the production of chloroprene which achieves a faster reaction speed while producing fewer undesirable byproducts is desired.

JP S46-19924 discloses a method for the production of chloroprene by reacting 3,4-dichloro-butene-1 and an alkali metal hydroxide in an aqueous medium in the presence of an organic catalyst, wherein said aqueous medium contains an amount of alkali metal hydroxide, computed by mass, which is sufficient to leave a final hydroxide concentration of at least 25% with respect to the total mass of water and hydroxide used. Said method is a method for the production of chloroprene which shows a fast reaction speed as well as extremely minimal production of undesirable byproducts. However, according to this method, chloroprene is removed from the reactants as a liquid, the aqueous phase and organic phase are separated and chloroprene is distilled from dichloro-butene, so a large amount of chloroprene polymerizes in the reactor used, resulting in losses and making it necessary to remove said polymer via separation; as a result, the apparatus used frequently becomes clogged and long term continuous operation is substantially difficult.

Additionally, this method does not specify how salt water (which contains primarily unreacted alkali metal hydroxide and produced alkali metal chloride as well as a small amount of organic components) left over

following the removal of chloroprene from the reaction mixture is processed and according to typical methods said salt water is typically fed into a reservoir where it gradually seeps into the ground, but when this brine
5 is disposed of by injection into a new water stream or salt water stream, alkali metal hydroxide contained in the aqueous solution at a concentration of 25% or greater is discarded, creating a significant economic problem as well as a large environmental problem.

10 JP S46-9846 discloses a method for the production of chloroprene in which 3,4-dichloro-butene-1 is reacted with an alkali metal hydroxide in an aqueous medium in the presence of a quaternary ammonium compound. Furthermore, JP S49-45379 discloses a method for the
15 production of chloroprene in which 3,4-dichloro-butene-1 is reacted with an alkali metal hydroxide in an aqueous medium in the presence of (1) a quaternary ammonium compound, (2) an amine oxide, (3) a sulfonium compound, or (4) a phosphate ester. These methods also
20 produce fast reaction times and the amount of the undesirable byproduct 1-chloro-butadiene-1,3 produced is small. Additionally, for these methods, as demonstrated by the figures contained in JP S46-19924, reaction speed is increased and production of the
25 byproduct 1-chloro-butadiene-1,3 is decreased the greater the initial concentration of alkali metal hydroxide aqueous solution used, which is desirable. The examples given in the specifications of these patents disclose nothing more than a batch reaction
30 method and do not show a process for the production of chloroprene which includes a method for extracting chloroprene from the reactor; if long term continuous operations are carried out using these methods, clogging due to chloroprene polymer cannot be avoided
35 and their industrial use is substantially difficult.

In order to render the production methods disclosed in JP S46-19924, JP S46-8846 and JP S49-45379 industrially useful, a process which limits the production of

polymers to a low level and includes a method for the extraction of chloroprene from the reactor, for which long term operation via the specified apparatus is not problematic over the long term, is needed.

5 The object of the present invention is the provision of a method for the production of chloroprene which shows a sufficiently high reaction speed, includes minimal production of undesirable byproducts such as 1-chloro-butadiene-1,3, includes minimal loss of alkali metal
10 hydroxide, does not produce wastewater during the dehydrochlorination process and does not readily result in clogging due to chloroprene polymer during long term continuous operation.

According to the method constituted by the present
15 invention, 3,4-dichloro-butene-1 is subjected to dehydrochlorination in an aqueous solution containing a relatively high concentration (25 - 55% by weight) of an alkali metal hydroxide in the presence of an organic catalyst, wherein a mixture containing chloroprene,
20 unreacted 3,4-dichloro-butene-1 and water produced by performing a reaction at a temperature of 20 - 100°C is removed in a gas phase via evaporation without reflux of said mixture into the reaction system, after which said evaporated mixture is completely condensed, said
25 condensed mixture is separated into an aqueous phase and an organic phase, after which said organic phase is subjected to fractional distillation to separate 3,4-dichloro-butene-1 and chloroprene; and wherein some water is evaporated away at a temperature of 95 - 100°C
30 from the water phase primarily containing an aqueous solution of alkali metal hydroxide and alkali metal chloride, which in turn contains solid alkali metal chloride obtained from the reaction, and the resulting material is concentrated to recover an aqueous solution
35 containing alkali metal hydroxide at a concentration of 15 - 55% by weight which is re-used in the reaction.

The alkali metal hydroxide used for the present invention is typically sodium hydroxide primarily for

economic reasons, but hydroxides of metals such as potassium, lithium, etc. can also be used.

The concentration of the alkali metal hydroxide used in the present invention ranges from 25 - 55% by weight.

5 If this concentration is less than 25%, not only is the speed of the reaction reduced, production of the byproduct 1-chloro-butadiene-1,3 is increased.

The reaction temperature ranges from 20 - 100°C; if the temperature is lower than 20°C the speed of the
10 reaction decreases. At temperatures higher than 100°C, separation of the byproduct 1-chloro-butadiene-1,3 becomes necessary, which renders the process uneconomical.

In order to rapidly distill chloroprene, which is
15 produced, from the reactor, the reactor can be heated via typical heating methods such as using a jacket to heat the reactor or blowing steam into the reactor. Additionally, if necessary, the alkali metal hydroxide aqueous solution, 3,4-dichloro-butene-1, etc. can be
20 fed into the reactor after being heated in advance.

A quaternary ammonium compound, quaternary phosphonium compound, quaternary sulfonium compound or mixture thereof is preferably used as an organic catalyst for the dehydrochlorination reaction. Examples of the above
25 include lauryl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, alkyl benzyl dimethyl ammonium chloride, octyl trimethyl ammonium chloride and octadecyl trimethyl ammonium chloride, but viable
30 examples are not limited to the above.

These catalysts are generally sold commercially dissolved in an alcohol solution, etc., and they may be used directly as a solution without first removing the solvent. Additionally, these catalysts may be used
35 after being dissolved in a solvent such as alcohol. The catalyst should preferably be used at a concentration of approximately 0.01 - 10% with respect to the weight of 3,4-dichloro-butene-1 used and the amount used

should be adjusted based on the activity of the catalyst used.

In order to avoid further reaction of chloroprene which is produced, the reaction should preferably be performed under an anoxic atmosphere or the reaction can be preferably carried out following the addition of a polymerization inhibitor such as phenothiazine.

Using the method constituted by the present invention, chloroprene which is produced is rapidly removed from the reactor via evaporation, so the undesired production of polymer resulting from extended contact with an alkaline aqueous solution is inhibited.

Maintaining an internal reactor pressure lower than atmospheric pressure is effective for increasing the speed at which chloroprene which is produced evaporates and the reaction can be suitably carried out under a pressure of 50 - 760 mmHg, depending on the reaction temperature.

Water is included in the organic phase separated along with the aqueous phase from the mixture obtained by completely condensing the evaporated mixture consisting of produced chloroprene, unreacted 3,4-dichloro-butene-1 and water in a settling tank, but drying the organic phase in advance via typical methods is effective in preventing corrosion of the distillation column as well as clogging of the distillation column due to the production of undesirable polymers during the separation of unreacted dichloro-butene and chloroprene. This drying process can vary according to the operating temperature of the distillation process, but typically drying until the water component contained in the organic phase is 0.04% by weight is sufficient, with a concentration of 0.01% by weight or less being preferable.

Chloroprene and 3,4-dichloro-butene-1 can be easily separated via distillation and it is possible to prevent the formation of polymer within the

distillation column, but vacuum distillation should preferably be performed.

Recovered 3,4-dichloro-butene-1 is re-used in the reaction.

5 Additionally, it is possible to extract 1-chloro-butadiene-1,3, which forms as a byproduct of dehydrochlorination, from the middle stage of the distillation column.

Some of the water is removed via evaporation from the
10 water phase containing primarily an aqueous solution of alkali metal hydroxide and alkali metal chloride, which in turn contains solid alkali metal chloride separated from the organic phase, and the resulting material is concentrated to recover alkali metal hydroxide.

15 Note that conventionally precipitation of dissolved alkali metal chloride accompanying the evaporation of this water as well as precipitation of polymer due to small amounts of 3,4-dichloro-butene-1, chloroprene and polymer contained in the aqueous phase are problematic.

20 Though it is possible to dissolve precipitants using water, as is typically done to avoid trouble arising from the precipitation of alkali metal chloride, trouble caused by polymer requires that the apparatus used be dismantled. As a result, concentration of
25 alkali metal hydroxide aqueous solution containing polymerizable organics, as is performed in the present invention, has not been previously carried out.

As a result of intensive investigations, it was discovered that when the operation is performed at a
30 temperature of 95°C or greater, it is possible to avoid trouble caused by polymer, even when a standard apparatus is used. If concentration is performed at a temperature lower than 95°C, within a short period of time, disassembly of the apparatus is required due to
35 deposition of polymer onto the apparatus. Additionally, operation at a temperature of 150°C or greater is not energy efficient and requires that expensive materials be used for the apparatus, which is not desirable.

Therefore, concentration performed within a range of 95 - 150°C is suitable.

Additionally, the method used to extract the organic phase in a gas phase according to the present invention is advantageous in that the load imposed during alkali concentration is lowered.

Solid alkali metal chloride is included in the water phase produced by the reaction and this solid component can be separated and removed or not separated and removed prior to the above concentration step. Furthermore, organic phase is somewhat mixed into the water phase, and this phase should preferably be concentrated following separation performed via standard methods such as leaving the mixture to stand. A forced circulation-type apparatus which inhibits boiling at the heat transfer surface is particularly preferred for use as the apparatus used in this concentration process for the purposes of inhibiting scale precipitation.

Example 1

Chloroprene was produced via the dehydrochlorination of 3,4-dichloro-butene-1 according to the process shown in the Figure. A mixture of fresh 3,4-dichloro-butene-1 derived from Conduit 1 and recovered 3,4-dichloro-butene-1 derived from Conduit 18, 50% by weight sodium hydroxide aqueous solution derived from Conduit 2 and the catalyst QUARTAMIN 24P (the brand name of lauryl trimethyl ammonium chloride sold by Kao Atlas Co., Ltd.) derived from Conduit 3 were fed into stirring machine-equipped Reactor 19 at rates of 100 parts per weight per hour, 76.8 parts per weight per hour and 1.0 parts per weight per hour respectively and a reaction was performed at 60°C and 225 mmHg (abs). The aqueous phase was extracted via Conduit 4 such that the level of Reactor 19 remained constant and the slightly mixed lipid and aqueous phases (including precipitated sodium chloride) were separated using Decanter 20, after which the lipid phase was returned to the reactor via Conduit

5. The aqueous phase containing solid sodium chloride from which the lipid phase was removed using Decanter 20 was fed into forced circulation-type Enricher 21 via Conduit 6 and concentration was carried out such that NaOH / (NaOH + H₂O) = 0.5 at 112°C and 200 mmHg (abs). After passing through Conduit 9 from Conduit 8, the aqueous phase was heated in Heat Exchanger 22 after which it was circulated into Enricher 21 via Conduit 10. As concentration was performed, dissolved sodium chloride precipitated out, but said aqueous phase was extracted via Conduit 8, directed into Slurry Tank 24 via Conduit 11 and fed into Centrifuge 25 where precipitated sodium chloride was separated out and also discarded via Conduit 12. Recovered sodium hydroxide aqueous solution was returned to Conduit 2 via Conduit 13 and fed back into the reaction. Additionally, in order to prevent clogging of the apparatus due to deposition of sodium chloride onto the walls of the enricher, warm water was fed into the enricher once every 8 hours to dissolve the deposited sodium chloride. At the same time, steam discharged from Enricher 21 was directed into Condenser 23 via Conduit 7, condensed and removed via Conduit 32 as water. Steam discharged from Reactor 19 was introduced into Condenser 26 via Conduit 14 and water separated out in Decanter 27 following condensation was removed via Conduit 15 and the remaining material was introduced into Dehydration Tower 28 via Conduit 16, after which it was fed into Distillation Column 29 following dehydration. The target chloroprene steam was extracted from the distillation column via Conduit 17 and condensed in Condenser 30 to obtain liquid chloroprene from Conduit 31. Unreacted 3,4-dichloro-butene-1 was extracted from the bottom of Distillation Column 29 and returned to Conduit 1 via Conduit 18 for re-use in the reaction.

The above procedure was continued for approximately 1 week with good separation of the lipid and aqueous

phases as well as no trouble with the enricher observed and the reaction rate of 3,4-dichloro-butene achieved was 98%.

Example 2

5 The same procedure as Example 1 was performed with the exception that the concentration of the sodium hydroxide aqueous solution was set to 30% by weight. In this example as well, the reaction was continued for 1 week and good separation of the lipid and aqueous
10 phases as well as no trouble with the enricher were observed.

Comparative Example 1

3,4-dichloro-butene-1, 50% by weight sodium hydroxide aqueous solution and QUARTAMIN 24P were fed into a
15 stirring machine-equipped reactor at rates of 100 parts per weight per hour, 76.8 parts per weight per hour and 1.0 parts per weight per hour respectively and a reaction was performed at 60°C. The reaction solution was extracted such that the level of the reactor
20 remained constant and an attempt was made to separate the lipid and aqueous phases, but no clear interface was observed and complete separation of the lipid and aqueous phases was substantially difficult. Additionally, the reaction rate of 3,4-dichloro-butene
25 achieved was 32.8%.

4. Brief Description of Figures

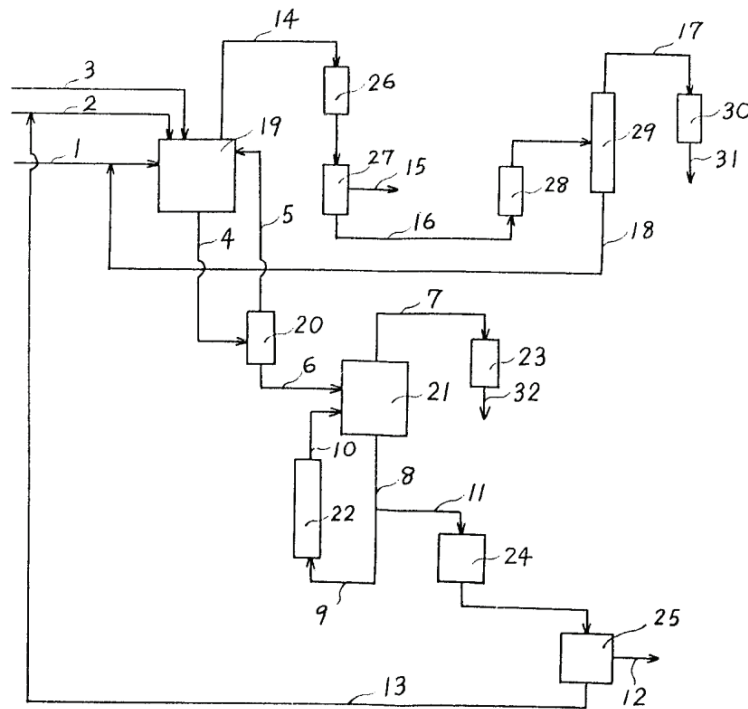
The Figure is a process diagram illustrating one embodiment of the present invention.

19...Reactor, 20...Decanter, 21...Forced Circulation Type
30 Condenser, 22...Heat Exchanger, 23...Condenser, 24...Slurry Tank, 25...Centrifuge, 26...Condenser, 27...Decanter, 28...Dehydration Tower, 29...Distillation Column, 30...Condenser

Patent Applicant: Denki Kagaku Kogyo Co., Ltd.

35

Figure



5

Procedural Amendments

November 24, 1982

To the Chief of the Patent Office: Kazuo WAKASUGI

10

1. Indication of Case

Patent Application No. 182624 of Showa Year 57 (1982)

2. Title of the Invention

A method for the production of chloroprene

15

3. Party Filing Amendment

Relation to Case: Patent Applicant

Address: 4-1 1-Chome, Yuraku-Cho, Chiyoda Ward, Tokyo

Name: (329) Denki Kagaku Kogyo Co., Ltd.

20

Representative Akira FUJIWARA [stamp]

4. Subject of the Amendment

Specification: Scope of the Patent Claims and Detailed Description of the Invention

5 5. Content of the Amendment

(1) The Scope of the Patent Claims is revised as per the separate sheet.

(2) Column 8, line 12 of the Specification is revised from "95 - 100°C" to "95 - 150°C".

10

Scope of the Patent Claims

1. A method for the production of chloroprene which is characterized in that chloroprene is produced by subjecting 3,4-dichloro-butene-1 to dehydrochlorination
15 in an aqueous solution containing 25 - 55% by weight of an alkali metal hydroxide in the presence of an organic catalyst, wherein a mixture containing chloroprene, unreacted 3,4-dichloro-butene-1 and water produced by performing a reaction at a temperature of 20 - 100°C is
20 removed in a gas phase via evaporation without reflux of said mixture into the reaction system, after which said evaporated mixture is completely condensed, said condensed mixture is separated into an aqueous phase and an organic phase, after which said organic phase is
25 subjected to fractional distillation to separate 3,4-dichloro-butene-1 and chloroprene; and wherein some water is evaporated away at 95 - 150°C from the water phase primarily containing an aqueous solution of alkali metal hydroxide and alkali metal chloride, which
30 in turn contains solid alkali metal chloride left over following removal of the reaction mixture in the gas phase via evaporation, and the resulting material is concentrated to recover an aqueous solution containing alkali metal hydroxide at a concentration of 15 - 55%
35 by weight which is re-used in the reaction.

2. A method for the production of chloroprene as specified in Claim 1 which is characterized in that, upon fractional distillation of the organic phase,

moisture is removed from said organic phase until moisture content is 0.04% by weight, after which the organic phase is subject to fractional distillation to separate 3,4-dichloro-butene-1 and chloroprene.

5 3. A method for the production of chloroprene as specified in Claim 1 which is characterized in that some water is evaporated from the water phase containing primarily an aqueous solution of alkali metal hydroxide and alkali metal chloride, which in
10 turn contains solid alkali metal chloride, and the resulting material is concentrated using a forced circulation concentration apparatus to recover alkali metal hydroxide which is reused in the reaction.

4. A method for the production of chloroprene as
15 specified in Claim 1 or Claim 3 which is characterized in that once the organic phase is separated from the aqueous phase containing primarily an aqueous solution of alkali metal hydroxide and alkali metal chloride, which in turn contains solid alkali metal chloride,
20 some water is evaporated and condensed.

5. A method for the production of chloroprene as specified in Claim 1 which is characterized in that recovered 3,4-dichloro-butene-1 is fed back into the dehydrochlorination reaction for reuse.

25 6. A method for the production of chloroprene as specified in Claims 1, 3 or 4 which is characterized in that solid alkali metal chloride is separated from an aqueous solution containing primarily alkali metal hydroxide and alkali metal chloride, which contains
30 solid alkali metal chloride, obtained following evaporation of part of the water component and concentration of the resulting material, after which a recovered aqueous solution composed primarily of alkali metal hydroxide and alkali metal chloride is fed back
35 into the dehydrochlorination reaction for reuse.

7. A method for the production of chloroprene as specified in Claim 1 in which a quaternary ammonium compound, quaternary phosphonium compound, sulfonium

compound or mixture thereof is used as a reaction catalyst.

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

ARKEMA FRANCE,

Petitioner,

v.

HONEYWELL INTERNATIONAL, INC.,

Patent Owner.

IPR No. IPR2015-00916

U.S. Patent No. 8,710,282

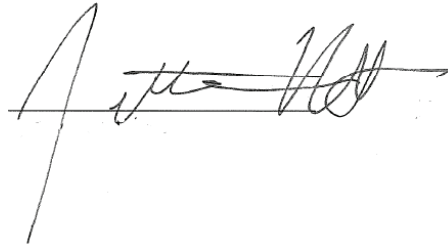
DECLARATION OF JONATHAN KENT

I, Jonathan Kent, hereby declare under penalty of perjury under the laws of the United States that the following statements are made based on personal knowledge and are true and correct:

1. I am fluent in both Japanese and English and have been employed as a professional translator for the past 10 years.

2. I prepared the attached document, which is a true and correct translation of Japanese Patent Application Publication No. S59-70626.

Date: 27th March 2015

A handwritten signature in black ink, appearing to read 'Jonathan Kent', is written over a horizontal line.

Jonathan Kent, BA, MA
Translator
RWS Group Ltd.