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Declaration under Rule 4.17:
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** METHOD FOR THE REGENERATION OF AQUEOUS LIQUIDS CONTAINING TRIMETHYL GLYCINE

(57) **Abstract:** The invention relates to a method for regenerating aqueous liquids containing trimethyl glycine and glycol, wherein said aqueous liquid containing trimethyl glycine and glycol is filtered and the filtrate a) is spray dried and optionally dried in a fluidized bed, or b) the filtrate is nanofiltered and optionally evaporated. Said liquid containing trimethyl glycine and glycol is a used functional liquid based on trimethyl glycine such as a cooling liquid for ice stadiums, a heat transfer liquid for technical building applications, an anti-freeze and thawing liquid for aircrafts and runways, or a cooling liquid for engines, or a mixture thereof.

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Method for the regeneration of aqueous liquids containing trimethyl glycine

Technical Field

The invention is directed to a method for regenerating trimethyl glycine and glycol containing aqueous heat transfer, cooling, anti-freeze, and thawing liquids for the reuse of trimethyl glycine. In this method, impurities, particles derived from the apparatuses and glycol typically originating from traditional glycol-based heat transfer and cooling liquids, are removed from used aqueous heat transfer, cooling, anti-freeze, and thawing liquids.

State of the Art

Heat transfer, cooling, anti-freeze, and thawing liquids based on trimethyl glycine, or betaine, contain trimethyl glycine as anhydrate or as monohydrate, or salts of trimethyl glycine such as hydrochloride, or derivatives of trimethyl glycine such as dimethylglycine, or mixtures thereof. Of these, trimethyl glycine monohydrate is the most widely used compound. Trimethyl glycine may be for instance produced synthetically or by extracting from natural sources such as from sugar beets.

Trimethyl glycine content in heat transfer, cooling, anti-freeze, and thawing liquids normally varies from 1 to 60 % by weight, the water content being from 40 to 99 % by weight. Moreover, the liquids may also contain adjuvants, for instance corrosion inhibitors, depending on the application.

Exhausted, or used, functional liquids based on trimethyl glycine, for instance cooling liquids for ice stadiums, heat transfer liquids for technical building applications, anti-freeze and thawing liquids for aircrafts and runways, and cooling liquids for cars are normally disposed of. Used liquids based on trimethyl

glycine typically contain various impurities, metal particles, such as iron, manganese, magnesium, aluminium, chromium, and nickel particles as well as other solid particles derived from equipment, and glycol such as ethylene and propylene, or butylene glycols originating from liquids used earlier in the equipment. Since the liquids contain additives and/or residues detrimental to the environment, e.g. ethylene glycol, they must be disposed of as hazardous waste.

The aim of the environmentally sustainable development is to keep environmental loads as low as possible. Accordingly, the disposal of heat transfer and cooling liquids by passing them to waste waters is not desirable.

A method for crystallizing trimethyl glycine from supersaturated aqueous solutions is known from EP 1177208.

Thus, on the basis of the above, there is an obvious need for a method for regenerating functional liquids containing trimethyl glycine and glycol, for instance various cooling liquids, heat transfer liquids for technical building applications, anti-freezing and thawing liquids for aircrafts and runways, and cooling liquids for engines, such as for vehicle engines, for the reuse of trimethyl glycine.

Objects of the Invention

An object of the invention is a method for regenerating aqueous solutions containing trimethyl glycine and glycol for the reuse of trimethyl glycine.

Another object of the invention is also the recovery of dry trimethyl glycine from used aqueous solutions containing trimethyl glycine and glycol for the reuse of trimethyl glycine.

Still another object of the invention is a recycling system for trimethyl glycine.

Characteristic features of the method and recycling system of the invention are presented in the Claims.

Summary of the Invention

The present invention is directed to a method for regenerating aqueous liquids containing trimethyl glycine and glycol, the method comprising filtration for the removal of solid matter and colour contained in the liquid, and a) spray drying and optional drying in a fluidized bed, or b) nanofiltration and optional evaporation.

More specifically, the invention is directed to a method for regenerating aqueous liquids containing trimethyl glycine and glycol, wherein said aqueous liquid containing trimethyl glycine and glycol is filtered and the filtrate a) is spray dried and optionally dried in a fluidized bed, or b) the filtrate is nanofiltered using a negatively charged membrane material and optionally evaporated, resulting in regenerated trimethyl glycine containing less than 0.5 % by weight of glycol.

Figures

The invention is illustrated by the appended Figures 1 and 2, without limiting the invention to the embodiments shown.

Figure 1 shows the method of the invention wherein used aqueous liquid containing trimethyl glycine and glycol is passed as stream 1 to the filtration step 10 for separating particles with particle sizes between 0.1 and 50 μm. In this step, litter, metal particles, compounds bound to iron, and colouring pigments are removed from the liquid. Following filtration, the filtrate is passed as stream 2 to a spray dryer 20 also receiving warm drying gas as stream 3. The drying gas, preferably air, is circulated as stream 4 through a cyclone 30 separating solid trimethyl glycine particles to a heating device 40 and returned to the spray dryer 20. From the bottom of the spray dryer 20, powdery trimethyl glycine is recovered

and pooled with the trimethyl glycine particles separated in the cyclone 30 as stream 7. The recovered trimethyl glycine is passed as stream 5 optionally to the fluidized bed dryer 50 wherein residual water is evaporated and remaining glycol residues are removed. Powdery trimethyl glycine is obtained in the stream 6 as the product that may be reused as such for producing for instance heat transfer liquids and cooling liquids.

Figure 2 shows another embodiment of the invention wherein used aqueous liquid containing trimethyl glycine and glycol is passed as the stream 1 to the filtration step 10 for separating particles with particle sizes between 0.1 and 50 μm. In this step, litter, metal particles, compounds bound to iron, and colouring pigments are removed from the liquid. Following filtration, the filtrate is passed as stream 2, and water as stream 4 and optionally the circulated water as stream 3 to a nanofilter 20 giving a concentrate containing trimethyl glycine as stream 6, and a filtrate 7 containing glycol and water. The concentrate containing trimethyl glycine, and water, respectively obtained as streams 6 and 5, are passed as pooled stream 11 to another nanofilter 30 giving a concentrate stream 8 containing trimethyl glycine, and a filtrate 9 containing glycol and water. The concentrate stream 8 containing trimethyl glycine obtained as the product may either be used as such for producing heat transfer or cooling liquids, or it may be concentrated by evaporation of the excessive water in an evaporator 40, or added with pure trimethyl glycine to attain the concentration desired for the working liquid.

Detailed Description of the Invention

Surprisingly, it was found that used functional liquids to be disposed of, based on trimethyl glycine and containing glycol, such as cooling liquids for ice stadiums, heat transfer liquids for technical building applications, anti-freeze and thawing liquids for aircrafts and runways, and cooling liquids for engines, such as vehicle engines, and the like, may be regenerated and the trimethyl glycine contained therein may be recovered for reuse with the method of the invention.

In this context, trimethyl glycine means the anhydrate and monohydrate of trimethyl glycine, salts of trimethyl glycine such as hydrochloride, derivatives of trimethyl glycine such as dimethyl glycine, and mixtures thereof. Of these, trimethyl glycine monohydrate is the most widely used compound.

In the method of the invention the used functional aqueous liquid, based on trimethyl glycine and containing glycol, such as a cooling liquid for ice stadiums, a heat transfer liquid for technical building applications, an anti-freeze and thawing liquid for aircrafts and runways, or a cooling liquid for engines, such as vehicle engines, or a mixture thereof is filtered for removing solid matter contained therein and the filtrate a) is spray dried and optionally dried in a fluidized bed, or b) the filtrate is nanofiltered and optionally evaporated.

In the first embodiment of the method of the invention, the used aqueous liquid containing trimethyl glycine and glycol, such as a heat transfer liquid is first filtered with one or several filters having a pore size from 0.1 to 50 μm, preferably from 0.5 to 20 μm. Then, according to the step a) of the method of the invention, the filtrate is passed to a spray dryer for spraying into drying gas in a hot chamber according to the spray drying technique to give small droplets with a droplet size less than 100 μm, thus allowing for the evaporation of the impurity components from the liquid by means of efficient mass transfer.

The drying gas may comprise air or nitrogen, preferably air. In case the equipment has a closed circulation, nitrogen is used. The temperature of the drying gas ranges from 160 to 280 °C, preferably from 190 to 240 °C. As the spray dryer, spray dryers of the prior art may be used. During spray drying, water and part of the glycols are evaporated from the filtrate, and crystallized dry trimethyl glycine powder is obtained as the product. Drying gas may either be circulated from the spray dryer through the cyclone and heater back to the dryer, or it may be passed without circulating directly to a gas washing unit operating according to conventional spray technique. The temperature of the air leaving the spray dryer is

typically between 95 and 160 °C, and that of the dry trimethyl glycine powder, obtained as the product, ranges from 50 to 80 °C.

For the spraying of the solution, a rotating disc nozzle or a pneumatic nozzle is used for efficient droplet formation and for obtaining an efficient mass transfer surface. With the pneumatic nozzle, the feed is preferably nebulized by means of hot air, thus promoting the evaporation of glycol in the spray. The rotating disc nozzle breaks the solution into small droplets preferably at 25000 rmp at the circumference of the rotating disc by means of centrifugal force, and further, mass transfer of the volatile components of the droplets may also be improved with introduced hot gas. In a known manner, also pressure nozzles may be used as nozzles.

Following spray drying, the trimethyl glycine powder is optionally passed to a fluidized bed dryer at a temperature ranging between 60 and 120 °C, preferably between 70 and 100 °C, wherein glycol remaining in trimethyl glycine is separated by fluidizing in the air. Glycol content in trimethyl glycine following drying is no more than 0.5 % by weight, and trimethyl glycine thus obtained is suitable as such for the production of heat transfer, cooling, and anti-freeze liquids.

In the alternative embodiment of the method of the invention, the used aqueous liquid based on trimethyl glycine and containing glycol is first filtered with one or several filters having a pore size from 0.1 to 50 μm, preferably from 0.5 to 20 μm. Then, according to the step b) of the method of the invention, the filtrate is passed to a nanofiltration step wherein water, preferably ion exchanged water, or demineralized water produced with membrane separation or distillation processes, and/or circulated water recovered in the method, is added to dilute the trimethyl glycine to a concentration ranging from 1 to 7, preferably from 3 to 5 % by weight, followed by passing this diluted solution to a nanofilter for removing water and impurities and glycols dissolved therein from the solution to give a

solution leaving the nanofilter as a concentrate containing trimethyl glycine from 10 to 20, preferably from 10 to 15 % by weight.

This embodiment of the regeneration method utilizing nanofiltration is based on the use of a semi-permeable and selective membrane material for separating trimethyl glycine from water and glycols. Nanofiltration membranes wherein the driving force for the separation is a pressure difference across the membrane are used as the separating membrane, or membrane material. In nanofiltration, trimethyl glycine is concentrated to a concentration between 10 and 20 % by weight at a pressure of 1500 – 8000 kPa (abs.) and at a temperature of 15 – 50 °C.

The pore size of nanofiltration membranes is greater than that of membranes for reversed osmosis, being typically from 0.5 to 2 nm, the membranes thus retaining components with molecular weights ranging from values more than 100 to 1000 daltons; dalton is a measuring unit proportional to molecular weight used in the membrane field for the separating power of membranes. Due to larger pore size, lower pressure differences across the membrane may be used in nanofiltration, thus saving enery. The molecular weight of trimethyl glycine is 117 g/mol, but however, nanofiltration may be utilized. It is preferable to use negatively charged nanofiltration membranes, thus allowing for the separation to be carried out at pressure levels lower than those necessary for reversed osmosis. The pore size of reversed osmosis membranes is typically less than 5 nm, the membranes thus retaining components with molecular weights higher than 10 – 100 daltons.

In the method of the invention utilizing nanofiltration, one or more sequential nanofiltration steps are used, the number thereof being preferably two, thus allowing for the removal of 80 – 90 % by weight of glycol, and accordingly the glycol content in the purified trimethyl glycine solution is from 0.1 to 0.3 % by weight, yield of the trimethyl glycine recovery being from 90 to 95 %. In the nanofiltration step, the temperature ranges between 15 and 50 °C, preferably from

20 to 40 °C, the operation pressure ranging from 1500 to 8000 kPa (abs.), preferably from 2000 to 4000 kPa (abs.).

In each nanofiltration step, the solution to be regenerated is first diluted with water, preferably using diafiltration or concentration to a desired concentration to lower the osmotic pressure of trimethyl glycine and to dissolve impurities in water. Said water is preferably ion exchanged water, or demineralized water produced with membrane separation or distillation processes. Thereafter, the solution thus obtained is passed to a nanofiltration unit wherein water and glycol dissolved in water pass the membrane, while trimethyl glycine is retained by the membrane.

In theory, the solution may be concentrated with respect to trimethyl glycine to a level where the osmotic pressure of the solution is the same as the operation pressure. In practice, however, an economical concentration level is significantly lower than this. Following nanofiltration steps, the regenerated trimethyl glycine solution may optionally be concentrated either by evaporation of the excessive water, or by the addition of pure trimethyl glycine to the solution.

The method of the invention has several advantages. By means of the method, pure trimethyl glycine can be separated as a powder, or regenerated trimethyl glycine may be recovered from exhausted heat transfer and cooling fluids for reuse. Moreover, impurities and glycol residues remaining in trimethyl glycine crystals may be effectively removed. Circulated trimethyl glycine, or an aqueous solution containing trimethyl glycine thus obtained may for instance be reused for the production of heat transfer and cooling liquids.

In the embodiment of the method of the invention utilizing spray drying, the product is directly obtained in a solid form allowing for the preparation of aqueous solutions necessary in various applications. If spray drying is used in

combination with a gas washer, glycols and other compounds detrimental to the environment may be removed.

The embodiment of the method of the invention utilizing nanofiltration is advantageous for the process safety since there are neither inflammable, or explosive gasses nor any risk of a dust explosion in the process.

The method of the invention allows for the controlled and economical recovery of the components to be removed and efficient yield of the purified product as a dry powder from a closed spray apparatus system.

The trimethyl glycine obtained with the method is suitable as such for reuse in functional liquids such as cooling liquids for ice stadiums, heat transfer liquids for technical building applications, anti-freeze and thawing liquids for aircrafts and runways, and cooling liquids for engines, such as vehicle engines, and the like applications. In this way, valuable trimethyl glycine may be recycled and utilized as a raw material, and further, environmental load may be reduced and sustainable development supported. Moreover, considerable savings with respect to raw materials are made in the production of liquids.

The invention is now illustrated with the following examples without wishing to limit the scope thereof.

Examples

Example 1

Filtration of a used cooling liquid containing trimethyl glycine for the removal of solid matter and colour

Test solution was a heat transfer liquid containing 49.5 % by weight of water, 46 % by weight of trimethyl glycine, 4 % by weight of ethylene glycol, and further,

solid impurities, used for 5 years in an ice stadium. The solution was passed to a 0.5 μm filter for efficient filtering of iron and other solid particles from the dark brown coloured feed to give a clear filtrate having light brown colour typical for trimethyl glycine.

Example 2

Regneration of an aqueous trimethyl glycine solution by spray drying

A heat transfer liquid containing 49.5 % by weight of water, 46 % by weight of trimethyl glycine, 4 % by weight of ethylene glycol, and further, solid impurities used for 5 years in an ice stadium was passed to a spray dryer. The solution was passed to a spray dryer and air at 230 °C was used as the drying gas. Trimethyl glycine powder containing 0.5 % by weight of water, and 1.5 % by weight of glycol was obtained as the product. The powder was then passed to a fluidized bed dryer wherein the temperature of the drying air was 70 °C. Trimethyl glycine powder containing less than 0.5 % by weight of glycol was obtained as the product.

Example 3

Membrane separation of trimethyl glycine and ethylene glycol from an aqueous solution

Separation of trimethyl glycine and ethylene glycol was studied using a DSS Labstak M20 –equipment with four different commercial membranes for reversed osmosis and nanofiltration. A test run was carried out with the equipment, using an aqueous solution containing 5 % by weight of trimethyl glycine and 0.3 % by weight of ethylene glycol as the starting solution. The test solution was prepared in water with a conductivity of < 2 μS/cm. The test run was carried out by recycling the concentrate of the equipment to the feed tank and by removing the permeate from the equipment of the test system. During testing, the temperature was 25 °C, and the operation pressure was elevated from the initial pressure of 20

bar (gauge) to the final pressure of 36 bar (gauge). The permeate pressure was normal atmospheric pressure. During testing, the concentration in the feed tank was monitored by measuring the solid matter content with a refractometer. Permeate flux was monitored during the test, and samples were taken from the permeate and feed at different pressure levels. Table 1 shows retentions calculated from the concentrate samples 20 bar (gauge), and 36 bar (gauge) for the used membranes RO1 99.5 % salt (NaCl) retention, RO2 99.5 % salt (NaCl) retention, RO3 99 % salt (NaCl) retention, and NF1 96 % salt ($MgSO_4$) retention.

Retention R is calculated with the equation:

$$R = [1 - (c_p/c_f)] \times 100\ \%$$

wherein c_p represents the concentration of the permeate, and c_f represents the concentration of the feed.

Table 1

Retentions of trimethyl glycine and ethylene glycol in the concentration test for three reversed osmosis membranes and one nanofiltration membrane

Membrane	Retention of trimethyl glycine, %		Retention of ethylene glycol, %	
	23 barg	36 barg	23 barg	36 barg
RO1	99.1	98.2	61.5	34.1
RO2	95.0	90.7	51.3	34.1
RO3	99.3	98.5	56.4	18.2
NF1	98.1	95.9	0.0	-22.7

As Table 1 indicates, retention of trimethyl glycine is high for reversed osmosis membranes (RO1, RO2, RO3), retentions of ethylene glycol being, however, also significant. In case of the nanofiltration membrane (NF1), ethylene glycol is

passed through with water, and at higher pressure levels, ethylege glycol may even be concentrated in the permeate.

Claims

1. Method for regenerating aqueous liquids containing trimethyl glycine and glycol, characterized in that the aqueous liquid containing trimethyl glycine and glycol is filtered and the filtrate a) is spray dried and optionally dried in a fluidized bed, or b) the filtrate is nanofiltered using a negatively charged membrane material and optionally evaporated, resulting in regenerated trimethyl glycine containing less than 0.5 % by weight of glycol.

2. Method according to Claim 1, characterized in that the aqueous liquid containing trimethyl glycine and glycol is a functional liquid such as a cooling liquid for ice stadiums, a heat transfer liquid for technical building applications, an anti-freeze and thawing liquid for aircrafts and runways, a cooling liquid for engines, or a mixture thereof.

3. Method according to Claim 1 or 2, characterized in that the aqueous liquid is filtered with one or several filters having pore sizes from 0.1 – 50 μm, preferably from 0.5 to 20 μm, followed by passing the filtrate to a spray dryer for spraying into a drying gas having a temperature between 160 and 280 °C, preferably 190 and 240 °C, and then, following spray drying, the resulting trimethyl glycine powder is optionally passed to a fluidized bed dryer at 60 – 120 °C, preferably at 70 – 100 °C.

4. Method according to any one of Claims 1-3, characterized in that the drying gas in the spray dryer is air or nitrogen, preferably air.

5. Method according to Claim 1 or 2, characterized in that the aqueous liquid is filtered with one or several filters having pore sizes from 0.1 – 50 μm, preferably from 0.5 to 20 μm, followed by passing the filtrate to a nanofiltration step wherein water, and optionally circulated water recovered in the method is added to the filtrate to dilute the trimethyl glycine to a concentration ranging from 1 to 7,

preferably from 3 to 5 % by weight, followed by passing this solution to a nanofilter for removing water and impurities dissolved therein from the solution to give a solution leaving the nanofilter as a concentrate containing trimethyl glycine from 10 to 20, preferably from 10 to 15 % by weight, optionally evaporating said solution thus obtained.

6. Method according to any one of Claims 1, 2 or 5, characterized in the said method comprises one or more nanofiltration steps at a temperature ranging from 15 to 50 °C, preferably from 20 to 40 °C, the operation pressure being from 1500 to 8000 kPa (abs), preferably from 2000 to 4000 kPa (abs).

7. Method according to any one of Claims 1, 2, 5 or 6, characterized in that the water is ion-exchanged water or demineralized water produced by membrane separation processes or distillation.

8. Method according to any one of Claims 1, 2, 5, 6 or 7, characterized in that water is evaporated from said regenerated trimethyl glycine solution, or pure trimethyl glycine is added to said trimethyl glycine solution to adjust the concentration as desired for a working solution.

9. Method for recycling used aqueous liquids containing trimethyl glycine and glycol, characterized in that the aqueous liquids containing trimethyl glycine and glycol are treated with the method according to any one of Claims 1 – 8, and functional liquids such as cooling liquids for ice stadiums, heat transfer liquids for technical building applications, anti-freeze and thawing liquids for aircrafts and runways, or cooling liquids for engines are produced from the resulting trimethyl glycine product, or from trimethyl glycine.

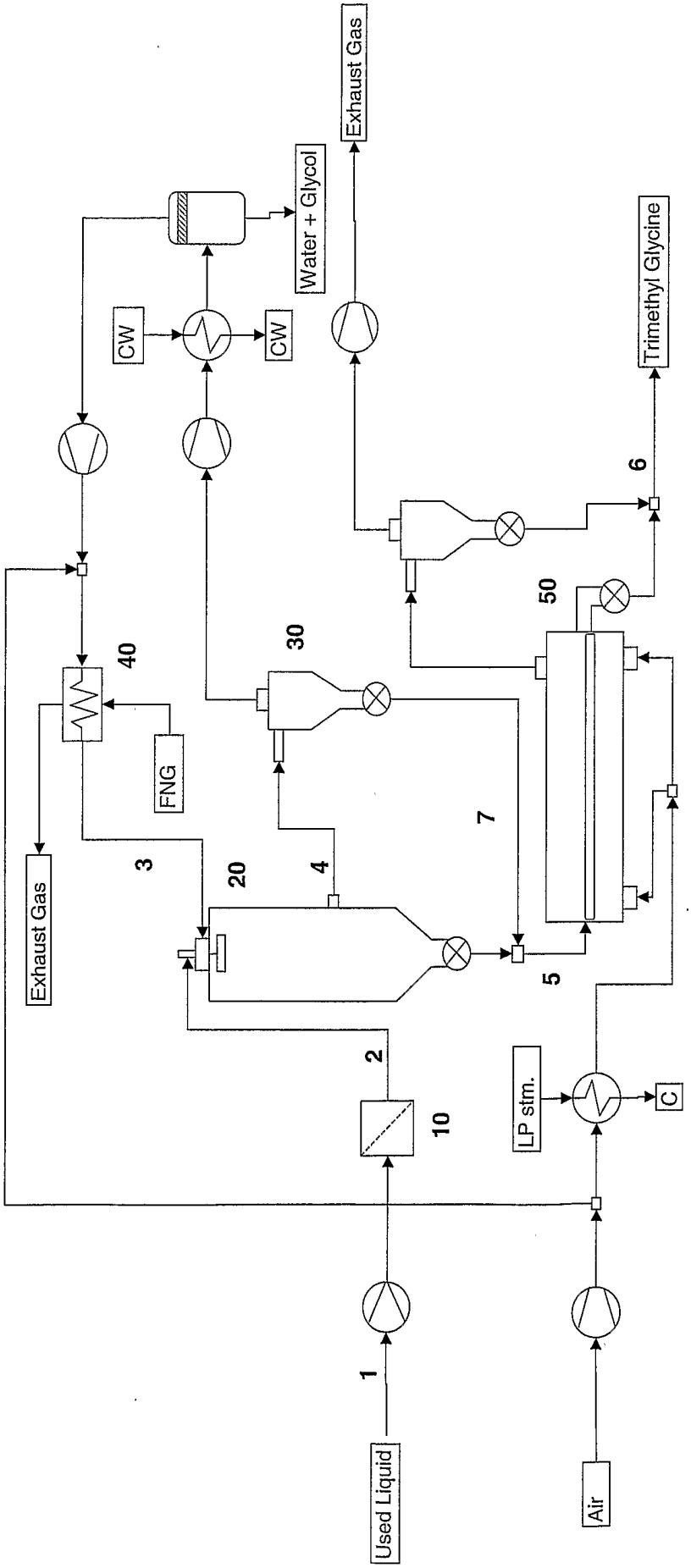
Exhaust Gas
Water + Glycol
CW
CW
Trimethyl Glycine
6
50
40
30
FNG
7
3
20
4
Exhaust Gas
5
2
10
LP stm.
C
1
Used Liquid
Air

FIG. 1

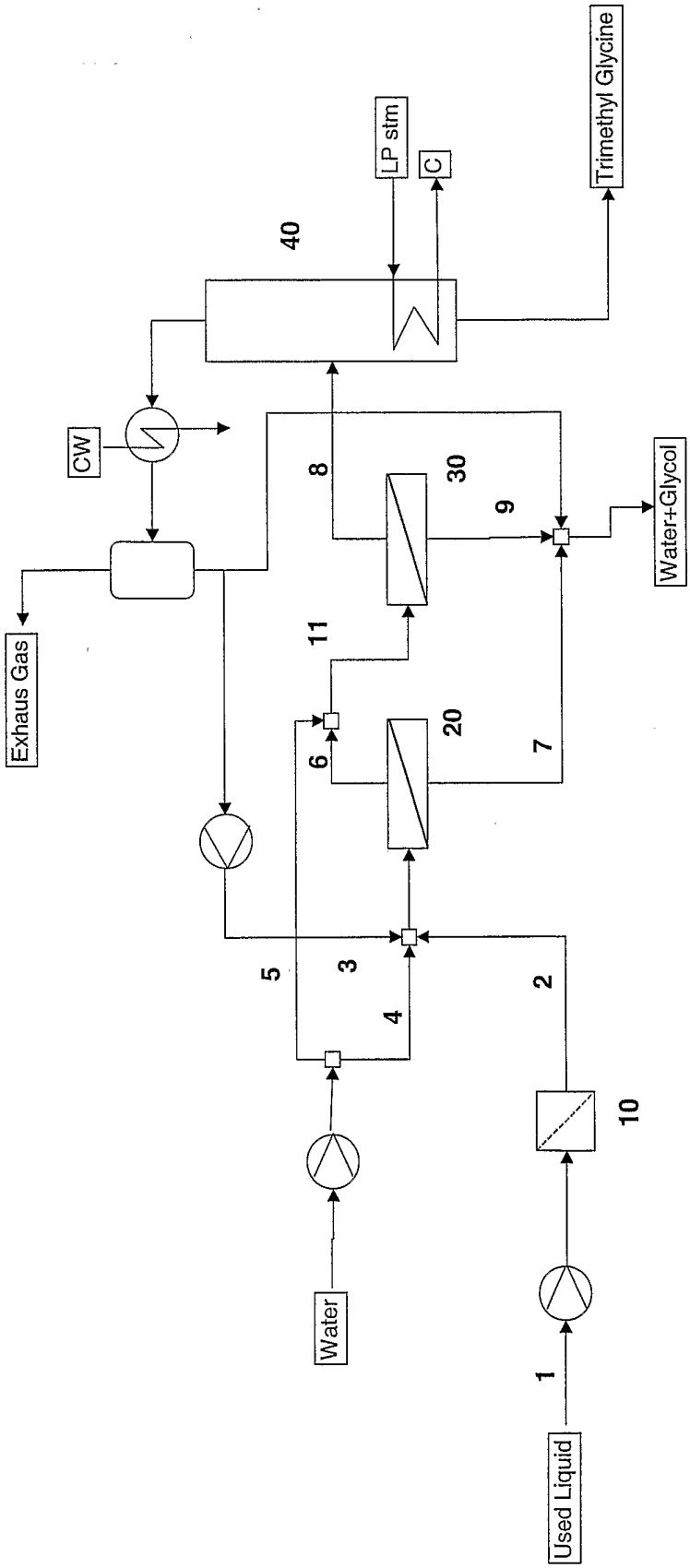
Trimethyl Glycine
LP stm
C
40
CW
8
30
9
Water+Glycol
Exhaus Gas
11
20
6
7
5
3
4
2
10
Water
1
Used Liquid

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2005/050483

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1) Claims 1a, 2-4, and 9

2) Claims 1b, 2, and 5-9

Invention 1 utilizes spray-drying and invention 2 nanofiltration for the regeneration of aqueous trimethylglycine liquids contaminated by glycols.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2005/050483

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8: C07C, C09K, B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO Internal, WPI, CHEM.ABS.DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02081381 A1 (COGNIS DEUTSCHLAND GMBH et al.) 17 October 2002 (17.10.2002), as a whole, especially claims 1, 4, and 7	1a
A	US 5411668 A (POELLMANN KLAUS et al.) 02 May 1995 (02.05.1995), as a whole	1b, 2, 5-9
A	WO 02053781 A1 (DANISCO SWEETENERS OY et al.) 11 July 2002 (11.07.2002), as a whole, especially claims 1, 10, and 62	1b, 5-8
A	WO 03040380 A2 (MESSO CHEMIETECHNIK GMBH et al.) 15 May 2003 (15.05.2003), as a whole, especially page 4, paragraph 3	1b, 5-8
A	WO 2004002938 A1 (FINNFEEDS FINLAND OY et al.) 08 January 2004 (08.01.2004), as a whole	1b, 5-8
A	US 5654480 A (DAHANAYAKE MANILAL S et al.) 05 August 1997 (05.08.1997), as a whole, especially formula I and column 3, lines 3-17	1b, 5-8

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 March 2006 (14.03.2006)	21 March 2006 (21.03.2006)

Name and mailing address of the ISA/FI
National Board of Patents and Registration of Finland
P.O. Box 1160, FI-00101 HELSINKI, Finland
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Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2005/050483

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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