

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C10M 105/58, 133/04	A1	(11) International Publication Number: WO 93/07241 (43) International Publication Date: 15 April 1993 (15.04.93)
(21) International Application Number: PCT/SE92/00701 (22) International Filing Date: 7 October 1992 (07.10.92) (30) Priority data: 9102931-4 10 October 1991 (10.10.91) SE (71) Applicant (for all designated States except US): BEROL NOBEL AB [SE/SE]; S-444 85 Stenungsund (SE). (72) Inventor; and (75) Inventor/Applicant (for US only) : SKÖLD, Rolf [SE/SE]; Dragonvägen 11, S-444 41 Stenungsund (SE). (74) Common Representative: ANDERSSON, Rolf; Berol Nobel AB, S-444 85 Stenungsund (SE).		(81) Designated States: CA, FI, JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: USE OF A TRIETHANOLAMINE PRODUCT MIXTURE (57) Abstract Use of a triethanolamine product mixture in cosmetic products, cleaning compositions and functional fluids, the triethanolamine product mixture containing a major part of triethanolamine, a minor part of diethanolmono-C ₃ -C ₄ -alkanolamine and monoethanoldi-C ₃ -C ₄ -alkanolamine and less than 1 % by weight diethanolamine and monoethanolamine.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SK	Slovak Republic
CI	Côte d'Ivoire	LK	Sri Lanka	SN	Senegal
CM	Cameroon	LU	Luxembourg	SU	Soviet Union
CS	Czechoslovakia	MC	Monaco	TD	Chad
CZ	Czech Republic	MG	Madagascar	TG	Togo
DE	Germany	ML	Mali	UA	Ukraine
DK	Denmark	MN	Mongolia	US	United States of America
ES	Spain			VN	Viet Nam
FI	Finland				

USE OF A TRIETHANOLAMINE PRODUCT MIXTURE

The present application relates to the use of a triethanol-
amine product mixture having a low content of diethanolamine
and monoethanolamine in functional fluids, such as lubricants,
metal working fluids and hydraulic fluids.

The use of triethanolamine in a variety of industrial
fluids is well known. Triethanolamines are normally produced in
one or more steps by ethoxylating ammonia with ethylene oxide.
In order to avoid the formation of polyalkyleneglycol chains,
 $\text{HOC}_2\text{H}_4(\text{OC}_2\text{H}_4)_n$, where $n > 0$, and the nitrogen atom to be quater-
nized the ethoxylation is normally stopped, when the reaction
mixture contains 60-90% by weight of triethanolamine and 10-40%
by weight of diethanolamine and monethanolamine. Such a reac-
tion mixture may be subjected to distillation to obtain purer
triethanolamine. The fact that the triethanolamine reaction
product contains a large amount of diethanolamine has not
previously been considered a real drawback, as diethanolamine
contributes to anticorrosion properties low foaming and desired
alkalinity when used in functional fluids.

Recently, more attention has been paid to the fact the
diethanolamine is toxic and forms nitrosamines, which are
carcinogenic in animal tests. Therefore, a reduction of the
content of diethanolamine is desirable. The content should
according to recommendations be less than 1% by weight.

Thus, one object of the invention is to produce a trietha-
nolamine product mixture which contains diethanolamine in an
amount less than 1% by weight. This triethanolamine product
mixture shall at least have about the same corrosion inhibiting
ability and/or defoaming properties in functional fluids.

Another object of the invention is that the method of
producing a triethanolamine product mixture shall be simple to
perform and that the mixture shall be usable without any
additional cleaning and/or working-up processes, such as
destillation.

Still another object of the invention is to keep the formation of quarternized triethanolamine and polyalkylene glycol chain containing ethanolamine products to a low level.

According to the invention it has now been found that these
5 objects can be met by using in functional fluids, a triethanolamine mixture containing a major part of triethanolamine, a minor part of diethanolmono-C₃₋₄-alkanolamine and monoethanoldi-C₃₋₄-alkanolamine, and less than 1% by weight of diethanolamine and monoethanolamine. By the expression "major part of tri-
10 ethanolamine" is here understood that said triethanolamine constitutes at least 50% by weight of the product mixture. The triethanol amine product mixture used in accordance with the invention can easily be obtained by reacting a conventional triethanolamine reaction mixture, obtained when reacting
15 ammonia in one or more steps, with a C₃-C₄-alkylene oxide.

Such a process is described in British Patent No 1 140 867. Diethanolamine and monoethanolamine which are both reactants in the process have a catalytic effect and catalyze rather selectively their own alkoxylation. The presence of an effective
20 amount of alkoxylation catalyst other than the diethanolamine and monoethanolamine shall preferably be avoided in order not to favour undesired side reactions. By the process the contents of diethanolamine and monoethanolamine are reduced to less than 1% by weight, while the undesired side reactions, such as
25 alkoxylation of hydroxyl groups or quarternization of the nitrogen atom is kept on a low level. In order to further suppress side reactions, it has been found suitable to perform the reaction below 160°C, preferably between 120-150°C. The amount of alkylene oxide added has to be adjusted in relation
30 to the amount of diethanolamine and monoethanolamine, so that the latter ones can be alkoxylated to the corresponding tertiary amine. Normally, the molar ratio of the alkylene oxide to the reactive hydrogen atoms bound to the nitrogen in diethanolamine and monoethanolamine is 1.0-1.4 and suitably 1.0-1.10.

35 The choice of alkylene oxide affects the HLB-value of the triethanolamine mixture formed during the reaction and the

butylene oxide may be preferred if a product mixture with the more hydrophobic and surface active character is desired.

Normally, the alkylene oxide used is propylene oxide. Both propylene oxide and butylene oxides react with a high selectivity with respect to the hydrogen atoms bound to the nitrogen atom in the primary and secondary amine resulting in a lower degree of side reactions like propoxylation of hydroxyl groups in monoethanolamine, diethanolamine or triethanolamine.

The triethanol amine product mixture used in accordance with the invention has many advantageous properties. Thus, application tests have clearly indicated that the triethanolamine product mixture is very suitable to replace triethanolamine as a component in aqueous functional fluids, such as lubricants, metal working fluids and hydraulic fluids. The diethanolmono-C₃-C₄-alkanolamine in the triethanolamine product mixture contributes to improved corrosion inhibiting and low foaming properties.

The present invention is further illustrated by the following examples.

Example A.

100 grams of a triethanolamine product mixture containing 85% by weight of triethanolamine and 15% by weight of diethanolamine and monoethanolamine (hereinafter referred to as TEA85) were reacted with 8,4 grams of propylene oxide at 60°C. The ratio between the molecules of propylene oxide and the number of hydrogen atoms bound to a nitrogen atom was 1,01. After all propylene oxide had reacted the product obtained (hereinafter referred to as TEA85+PO) was analyzed with respect to the presence of secondary and primary ethanolamines. The total content of these alkanolamines was found to be less than 0,5% by weight.

Example B.

100 grams of the same triethanolamine product mixture as specified in Example A were reacted with 10,4 grams of butylene oxide at 70°C. The ratio between the molecules of butylene oxide and the number of hydrogen atoms bound to a nitrogen atom

was 1,00. After reaction with product mixture obtained (hereinafter referred to as TEA85-BO) was analyzed and the content of secondary and primary alkanolamines was found to be 0,7% by weight.

5 **Example C.**

100 grams of the same triethanolamine products mixture as specified in Example A were reacted with 10.9 grams of propylene oxide at 150°C. The ratio between the molecules of propylene oxide and the number of hydrogen atoms bound to a nitrogen atom were 1.3. After reaction the content of secondary and primary alkanolamines was found to be less than 0.1% by weight.

Example 1.

The triethanolamine product mixtures TEA85-PO and TEA85-BO from Examples A and B were diluted with water having a water hardness of 0,2°dH to solutions containing 1, 2 and 3% by weight. The solutions were then neutralized with acetic acid to a pH-value of 9. As comparisons corresponding solution was also formulated from the triethanolamine product mixture used as starting product in Example A (hereinafter referred to as TEA85) and a distillation product of TEA85 containing 99% by weight of triethanolamine. The latter product are hereinafter referred to as TEA99.

The twelve solutions were then tested with regard to their Fe corrosion according to cast iron chip-on-filter paper test (IP 287) and copper corrosion. In the measuring of copper corrosion 0,2 grams of copper powder was mixed with 10 grams of glass beads in 200 ml of the solution containing the alkanolamines. The solutions were shaken for 24, 48 and 72 hours and the content of copper in the solutions was determined. The following results were obtained.

Alkanolamine	Fe corrosion		
	% of the filter paper stained		
	Concentration		
	1%	2%	3%
TEA85	70	50	40
TEA99	80	40	20
TEA85-PO	40	30	20
TEA85-BO	30	20	10

	Cu corrosion								
	Cu-content in the solution, ppm								
	1%			2%			3%		
Concentration									
Time, h	24	48	72	24	48	72	24	48	72
TEA85	150	250	300	200	250	300	200	250	300
TEA99	150	250	300	200	250	300	150	250	300
TEA85-PO	100	200	200	100	150	200	150	150	200
TEA85-BO	75	150	200	100	150	200	100	150	200

It is obvious that the alkanolamine product mixtures in accordance with the invention have favourable corrosion properties in comparison with prior used alkanolamine products.

Example 2.

The solutions of Example 1 containing 3% by weight of the alkanolamines were also tested with regard to foaming. 200 ml of each solution was vigorously stirred during 5 minutes and the volume of the fluid and the foam was measured. The following results were obtained.

5

Alkanolamine	Volume ¹⁾ of foam and fluid ml			
	Delay after stirring, min			
	0	1	2	3
TEA85	230	220	205	200
TEA99	230	225	210	200
TEA85-PO	205	200		
TEA85-BO	200			

10

¹⁾ Volume of the solutions before stirring is 200 ml.

From the results it is evident that the product mixtures of the invention has a low foaming like the prior art products.

Example 3.

15

20

Synthetic metal working fluid concentrates were prepared from 20 parts by weight of TEA85-PO or TEA99, 25 parts by weight of dodecandioic acid, 55 parts by weight of distilled water and potassium hydroxide in an amount sufficient to give a pH of 9,8. The concentrates were then diluted with water having a water hardness of 200 ppm in accordance with the table below and tested with regard of foaming ability in accordance with Institute of Petroleum, IP 312 and with regard to iron corrosion in the same manner as in Example 1. The following results were obtained.

5

Alkanol-amine	Dilution	Foaming		Fe-corrosion % of filter paper stained
		Initial foam heights, cm	Time to zero foam, s	
TEA99	1:20	20	15	-
TEA85-PO	1:20	20	8	-
TEA99	1:70	-	-	5
TEA85-PO	1:70	-	-	3

From the results it is evident that the triethanolamine product mixture of the invention with advantage can replace TEA99.

CLAIMS

- 5 1. Use of a triethanolamine product mixture in functional fluids, the triethanolamine product mixture containing a major part of triethanolamine, a minor part of diethanolmono-C₃-C₄-alkanolamine and monoethanoldi-C₃-C₄-alkanolamine and less than 1% by weight diethanolamine and monoethanolamine.
- 10 2. Use in accordance with claim 1, characterised in that the major part is 60-90% by weight, and the minor part is 10-40% by weight.
3. Use of the triethanolamine product mixture of claim 1 or 2 in an aqueous metal working fluid.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 92/00701

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 10 M 105/58, 133/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 10 M	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4273937 (MARY L. GUM ET AL.) 16 June 1981, see column 1; lines 5-8 and 18-19 --	1
A	US, A, 4420414 (FREDERICK W. VALONE) 13 December 1983, see column 1, line 5 - line 10 and line 57 - line 64 --	1
A	US, A, 4726914 (LARRY A. FELLOWS ET AL.) 23 February 1988, see claim 1 -- -----	1
* Special categories of cited documents:¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document 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 "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		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
18th January 1993	20 -01- 1993	
International Searching Authority	Signature of Authorized Officer	
SWEDISH PATENT OFFICE	Dagmar Järvman	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 92/00701

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 08/01/93. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4273937	81-06-16	CA-A- 1133516	82-10-12
		EP-A-B- 0031284	81-07-01
		JP-C- 1241722	84-11-26
		JP-A- 56092838	81-07-27
		JP-B- 59017102	84-04-19
US-A- 4420414	83-12-13	DE-A- 3411846	84-10-11
		GB-A-B- 2137976	84-10-17
US-A- 4726914	88-02-23	NONE	