



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B01D 17/00, 19/04, C08K 5/06 C08J 7/02	A1	(11) International Publication Number: WO 91/01171 (43) International Publication Date: 7 February 1991 (07.02.91)
<p>(21) International Application Number: PCT/US90/03895</p> <p>(22) International Filing Date: 11 July 1990 (11.07.90)</p> <p>(30) Priority data: 379,311 12 July 1989 (12.07.89) US</p> <p>(71) Applicant: GAF CHEMICALS CORPORATION [US/US]; 1361 Alps Road, Wayne, NJ 07470 (US).</p> <p>(72) Inventor: DAHANAYAKE, Manilal, S. ; 22 Ella Lane, Wayne, NJ 07470 (US).</p> <p>(74) Agent: VENTURINO, Anthony, P.; Morgan & Finnegan, 345 Park Avenue, New York, NY 10154 (US).</p>	<p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent)*, DK, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
(54) Title: LOW VISCOSITY DEFOAMING-ANTIFOAMING FORMULATIONS		
$\text{HO} \left(\text{CH}_2 \overset{\text{CH}_3}{\underset{ }{\text{CHO}}} \right)_a \left(\text{CH}_2 \text{CH}_2 \text{O} \right)_b \left(\text{CH}_2 \overset{\text{CH}_3}{\underset{ }{\text{CHO}}} \right)_c \text{H} \quad ; \quad (\text{I})$ $\text{HO} \left(\text{CH}_2 \text{CH}_2 \text{O} \right)_x \left(\text{CH}_2 \overset{\text{CH}_3}{\underset{ }{\text{CHO}}} \right)_y \left(\text{CH}_2 \text{CH}_2 \text{O} \right)_z \text{H} \quad (\text{II})$ $\text{HO} \left(\text{CH}_2 - \overset{\text{CH}_3}{\underset{ }{\text{CHO}}} \right)_d \text{H} \quad (\text{III})$		
(57) Abstract		
<p>The present invention relates to balanced hydrophobic/hydrophilic liquid formulations comprising: (a) between about 10 and about 90 % by weight of a block copolymer having formula (I) or (II), or a mixture thereof; (b) between about 90 and about 10 % by weight of a polypropylene glycol having formula (III), and (c) between about 0.3 and about 10 % by weight hydrophobic silica based on components (a) + (b). The invention also pertains to the use of the above mixture in foamed liquids or liquid susceptible to foaming. Also described are a process for inhibiting swelling in a polymer and the polymers produced by the process of inhibiting swelling.</p>		

DESIGNATIONS OF "DE"

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LOW VISCOSITY DEFOAMING/ANTIFOAMING FORMULATIONSPRIOR ART

The polypropylene glycols and polyoxyethylene-polyoxypropylene copolymers which have been employed individually as antifoaming agents have several drawbacks. Primarily, they have limited water solubility and dispersibility so that large amounts of these antifoamers must be employed and, even then, the defoaming action is relatively low. Generally, a foam head of less than 2 cm on a 60 square cm surface area is the upper limit of tolerance for commercial defoaming applications and for certain uses not more than 0.3 cm is required. Secondly, formulations containing these compounds are somewhat viscous which presents pumping difficulties in antifoaming processing. Several solid non-foaming dispersing formulations have also been proposed as in U.S. 3,959,176; however these present problems of dispersibility and cannot be pumped into foamable solutions.

Accordingly, it is an object of this invention to overcome the above deficiencies of the prior art and to provide a particularly effective antifoaming/defoaming mixture which is economically prepared.

Another object of this invention is to provide a liquid mixture which is capable of defoaming an aqueous system at a greatly increased rate.

Another object is to provide a liquid antifoaming/defoaming composition having significantly reduced viscosity which can be most economically incorporated into a foamable liquid or added to a foam.

Still another object is to prepare a composition which, in addition to its antifoaming and defoaming properties, provides anti-swelling in solutions of various polymers.

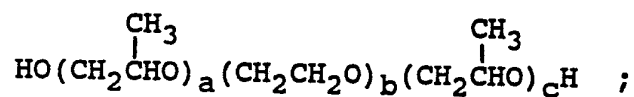
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These and other objects of the invention will become apparent from the following description and disclosure.

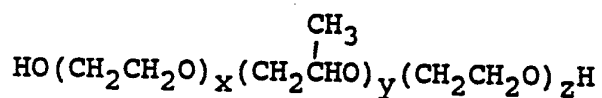
THE INVENTION

In accordance with this invention there is provided a liquid antifoaming/defoaming mixture or blend of components having a cloud point less than 35 and comprising:

(a) between about 10 and about 90% by weight of an alcohol alkoxyate having the formula

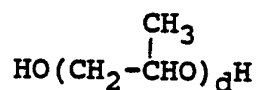


or



or a mixture thereof;

(b) between about 90 and about 10% by weight of polypropylene glycol having the formula



and

(c) between about 0.3 and about 10% by weight hydrophobic silica based on components (a) + (b),

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wherein the lettered subscripts have the following values:

the sum of $a + c = 10$ to 150 , preferably 20 to 70

$b = 2$ to 100 , preferably 4 to 20

$d = 15$ to 200 , preferably 25 to 100

the sum of $x + z = 2$ to 40 , preferably 4 to 15

$y = 30$ to 100 , preferably 40 to 80

The cloud points of instant mixtures are below 35 ; although a cloud point of from about 1 to about 25 is most beneficial.

Component (a) of the present composition is a copolymer having a number average molecular weight of between about 675 and about $15,000$, preferably between about $1,000$ and about $10,000$.

Preferred blends of the present composition are those wherein component (a) and component (b) are each present in an amount between about 35% and about 65% by weight; most preferred are those having about equal proportions of component (a) and component (b) and where propylene oxide units, with respect to ethylene oxide units, predominate in the overall composition. The hydrophobic silica is preferably employed at concentrations between about 0.1 and about 8% by weight, most desirably, when a liquid mixture having a viscosity of not more than 500 cps is required, the concentration of the silica is not greater than 5% by weight. Although the viscosity of the liquid mixture can vary between about 100 and about $5,000$ cps, depending upon its intended use, viscosities in the lower portion of this range, e.g. less than 500 cps, are

usually desired for processing purposes. While increased hydrophobic silica content materially raises the viscosity, such increased amounts do not provide any antifoaming benefit. Accordingly, the amount of hydrophobic silica above 10% by weight is not desirable.

The hydrophobic silica component of the composition, as known in the art, is prepared from hydrophilic silica which is treated to render the silica hydrophobic. One suitable method for rendering the silica hydrophobic is to permanently affix a liquid hydrophobic polysiloxane oil onto the silica particles. Since hydrophobic silica is well known in the art, no detailed description thereof is deemed necessary for a complete understanding of the present invention. The preparation of hydrophobic silica is described in U.S. Patent Nos. 3,207,698; 3,408,306; and 3,076,768, as well as the references referred to in such patents, all of which are hereby incorporated by reference. A preferred silica is a precipitated silica, such as the precipitated silica sold as Quso-G30 or Quso WR-83.

The above blend of components provides a hydrophobic/hydrophilic balance which allows faster diffusion of the antifoamer composition into the liquid/air interface and rapidly transports silica to the interface where a small amount efficiently performs defoaming action. The components of the above mixture also interact to effect deconstructurization of the monomolecular foamed layer by increasing the free energy of interaction between the foam forming molecules which leads to liberation of air and collapse of bubbles. Because of the hydrophobic/hydrophilic balance in the above formulation, the present composition has greater affinity for, and faster action in, aqueous systems which are subject to foaming. The present blend is capable of reducing the foam head of a foamed liquid by more than 70% upon contact and in less than 1.5 minutes completely destroying the foam.

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In addition to its defoaming and antifoaming functions, the present composition provides anti-swelling properties to certain polymers including polyvinyl halides, polypropylenes, polyethylenes, polytetrafluoroethylenes, polychlorotrifluoroethylenes and the like.

Examples of foamed or foamable solutions to which the present composition is applied, include the alkali and alkaline earth metal salts, as well as ammonium salts, of alkyl benzene sulfonates and lauryl sulfates, lauryl ether sulfates, alkoxyated alkyl phenols, urethane polymers, phosphate ester surfactants, salts of fatty acids employed in the paper making industry and photopolymers, such as methacrylic alkyl esters and their carboxylic salts, employed for printed board circuits in the electronic industry. The present blends are useful as defoamers or antifoamers for laundry detergents, dishwashing formulations, paper making processes, metal working processes and many others.

To effect defoaming or antifoaming only a small amount of the blend is needed to provide the desired result. Generally between about 0.001% and about 3% by weight, preferably between about 0.05% and about 0.5% by weight of the present blend, based on foamed or foamable liquid, is employed to defoam on contact. The present mixture is economically and conveniently prepared by merely mixing components (a), (b) and (c) in any order at a temperature between about 10°C. and about 100°C. under atmospheric conditions for a period of up to 3 hours depending upon the volume. Generally, the formulation is prepared within a 1 hour mixing period at ambient temperature depending upon the volume and the mixing equipment employed. The resulting mixture is preferably used in undiluted condition; although in certain cases

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where desired, it can be diluted to a desired concentration with an inert solvent such as water, PEG, PPG, benzene, heptane, hydrocarbons and the like before contact with a foamed layer or before admixture with a foamable liquid prior to agitation. The defoaming or antifoaming operations are carried out under the same conditions of temperature and pressure described above using conventional foam breaking or liquid mixing techniques.

Having generally described the invention, reference is now had to the accompanying examples which include preferred embodiments. These examples are not to be construed as limiting to the scope of the present antifoaming/defoaming and anti-swelling compositions which are more broadly set forth above and in the appended claims.

EXAMPLE 1

The following composition A was mixed for 5 minutes at ambient temperature under atmospheric conditions in a 200 ml glass beaker.

- (a) 50 g. of 10% polyoxyethylene-90% polyoxypropylene copolymer having polyoxyethylene capping blocks (PEGOL L-121) and having a molecular weight of 4,440.
- (b) 49 g. of polypropylene glycol having a molecular weight of 4,000 (ALKAPOL PPG 4000).
- (c) 1 g. of hydrophobic silica (QUSO WR-83).

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The antifoaming property of the above composition was tested as follows. As a control, 200 g. of 0.1% anionic dodecyl benzene sulfonate sodium salt in water was stirred at ambient temperature in a glass measuring column for 1 minute at 1000 rpm and developed a foam head of 10 cm. Stirring was then discontinued and the liquid left to stand for 1 minute. The foam head was unchanged after 1 minute standing time. The above procedure was repeated except that 0.1% of the above liquid composition was added to the sulfonate before stirring. After stirring this mixture for 1 minute, only 1.5 cm of foam head developed and after 1 minute standing time, the sulfonate was completely defoamed.

EXAMPLE 2

The antifoaming test of Example 1 was repeated except that a photopolymer, i.e. methacrylic acid methyl ester (RISTON in 0.85% Na_2CO_3), was substituted for the foamable sulfonate salt. The results were as follows

	<u>cm</u>
Initial foam head of photopolymer in absence of Composition A/foam head after 1 minute	3.1/2.8
Initial foam head of photopolymer containing 0.1% of Composition A/foam head after 1 minute	0.1/0.0

EXAMPLE 3

Example 1 was repeated except that the following composition (B) was substituted for composition (A).

- (a) 50 g. of 10% polyoxyethylene-90% polyoxypropylene copolymer having the polyoxypropylene capping blocks (PEGOL 31R1) and having a molecular weight of 3200.
- (b) 49 g. of polypropylene glycol having molecular weight of 4000 (ALKAPOL PPG 4000).
- (c) 1 g. of hydrophobic silica (QUSO WR-83)

The results of the antifoaming tests were as follows.

Initial foam head developed in the absence of Composition B/foam head after 1 minute	<u>cm</u> 10.0/10.0
Initial foam head developed in liquid incorporating 0.1% of Composition B/foam head after 1 minute	1.7/0.0

EXAMPLE 4

Example 1 was repeated except that the following composition (C) was substituted for composition (A).

- (a) 50 g. of 20% polyoxyethylene-80% polyoxypropylene copolymer having the polyoxypropylene capping blocks (PEGOL 25R2) and having a molecular weight of 3120.
- (b) 49 g. of polypropylene glycol having molecular weight of 4000 (ALKAPOL PPG 4000).
- (c) 1 g. of hydrophobic silica (QUSO WR-83)

The results of the antifoaming tests were as follows.

	<u>cm</u>
Initial foam head developed in the absence of Composition C/foam head after 1 minute	10.0/10.0
Initial foam head developed in liquid incorporating 0.1% of Composition C/foam head after 1 minute	1.8/0.1

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COMPARATIVE EXAMPLE 5

Example 1 was repeated except that the following composition (D) was substituted for composition (A).

- (a) 50 g. of 80% polyoxyethylene-20% polyoxypropylene copolymer having the polyoxypropylene capping blocks.
- (b) 49 g. of polypropylene glycol having molecular weight of 2000 (ALKAPOL PPG 2000).
- (c) 1 g. of hydrophobic silica (QUSO WR-83).

The results of the antifoaming tests were as follows.

Initial foam head developed in the absence of Composition D/foam head after 1 minute	<u>cm</u> 10.0/10.0
Initial foam head developed in liquid incorporating 0.1% of Composition D/foam head after 1 minute	5.6/4.5

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This example illustrates the affect of excess moles of polyoxyethylene in the overall composition.

COMPARATIVE EXAMPLE 6

Example 1 was repeated except that the following composition (E) was substituted for composition A.

- (a) 50 g. of polyoxyethylene (21 moles)
polyoxypropylene (16 moles) copolymer having
polyoxyethylene capping block groups (PEGOL L-35)
and having a molecular weight of 1900.
- (b) 49 g. of polypropylene glycol having a molecular
weight of 4000 (ALKAPOL PPG 4000).
- (c) 1 g. of hydrophobic silica (QUSO WR-83).

The results of the antifoaming tests were as follows.

Initial foam head developed in the absence of Composition E/foam head after 1 minute	<u>cm</u> 10.0/10.0
Initial foam head developed in liquid incorporating 0.1% of Composition E/foam head after 1 minute	5.2/4.5

This example illustrates the affect resulting from component (a) where subscript y has a value less than 30. As shown, the foam head was not reduced to an acceptable limit.

COMPARATIVE EXAMPLE 7

Example 1 was repeated except that the following composition (F) was substituted for composition A.

- (a) 45 g. of 10% polyoxyethylene-90% polyoxypropylene copolymer having polyoxyethylene capping blocks (PEGOL L-121).
- (b) 43 g. of polypropylene glycol having a molecular weight of 4000 (ALKAPOL PPG 4000).
- (c) 12 g. of hydrophobic silica (QUSO WR-83).

Composition F has a viscosity of 4,000 cps which clogged in the supply pump. Accordingly, the 0.1% addition to the foamable liquid was achieved manually with vigorous mixing for a period of more than 4 hours at 110°C. The results of the antifoaming tests are as follows.

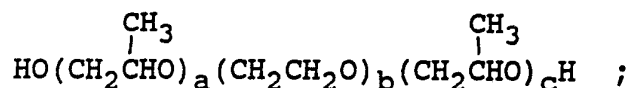
Initial foam head developed in the absence of Composition F/foam head after 1 minute	<u>cm</u> 10/10
Initial foam head developed in liquid + 0.1% of Composition F/foam head after 1 minute	1.5/0.0

Although composition F achieved good antifoaming, the mixture was highly viscous and could not be pumped into the foamable liquid.

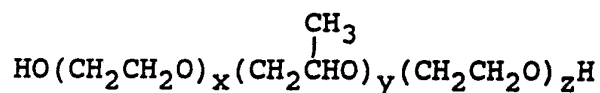
WHAT IS CLAIMED IS:

1. A defoaming/antifoaming liquid composition having a cloud point less than 35 and containing

(a) between about 10 and about 90% by weight of an alcohol alkoxyate having the formula

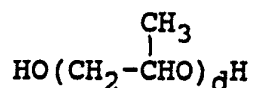


or



or a mixture thereof;

(b) between about 90 and about 10% by weight of polypropylene glycol having the formula



and

(c) between about 0.3 and about 10% by weight hydrophobic silica based on components (a) + (b),

wherein the lettered subscripts have the following values:

the sum of $a + c = 10$ to 150 ,

$b = 2$ to 100 ,

$d = 15$ to 200 ,

the sum of $x + z = 2$ to 40 ,

$y = 30$ to 100 .

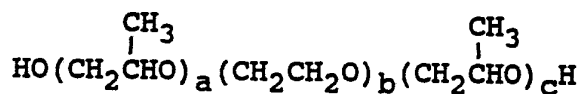
2. The composition of Claim 1 wherein component (a) and component (b) are each present in the mixture in an amount between about 35 and about 65 weight % and the concentration of the silica is between about 0.1 and about 8% and wherein the propylene oxide units, with respect to the ethylene oxide units, predominate in the overall composition.

3. The composition of Claim 1 wherein said mixture has a viscosity of between about 100 and about 3,000 cps.

4. The composition of Claim 3 wherein the mixture has a viscosity of not more than 500 cps.

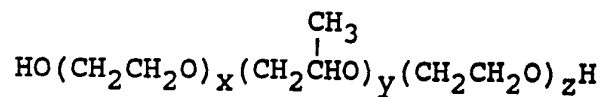
5. The composition of Claim 1 which has a cloud point between about 1 and about 25.

6. The composition of Claim 1 wherein component (a) is



and the sum of $a + c$ has a value of 20 to 70.

7. The composition of Claim 1 wherein component (a) is



and y has a value of 40 to 80.

8. The process of adding an effective antifoaming/defoaming amount of the composition of Claim 1 to a liquid subject to foaming.

9. The process of Claim 8 wherein between about 0.001% and about 3% by weight of the composition is added to said foamable liquid.

10. The process of adding an effective defoaming amount of the composition of Claim 1 to the air/liquid interface of a foamed liquid.

11. The process of Claim 10 wherein between about 0.001% and about 3% by weight of the composition is added to the foamed liquid.

12. A foamable liquid containing from about 0.001% and about 3% by weight of the mixture of Claim 1.

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13. The foamable liquid of Claim 12 containing from about 0.005% to about 0.5% by weight of said mixture.

14. The process of contacting a swellable polymer with an anti-swelling amount of the composition of Claim 1.

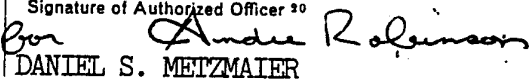
15. The process of Claim 14 wherein from about 0.001% to about 3% by weight of the composition of Claim 1 is contacted with the swellable polymer and the swellable polymer is a polyvinyl halide.

16. The product of the process of Claim 14.

17. The product of the process of Claim 15.

INTERNATIONAL SEARCH REPORT

International Application No **PCT/US90/03895**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(5): B01D 17/00, 19/04; C08K 5/06; C08J 7/02		
U.S. CL.: 252/321,358; 568/593; 524/377; 8/115.54		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	252/321, 358; 568/593, 602, 606, 619; 524/377; 8/115.54; 106/12, 387.34	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	CA, A, 1,143,244 (DIVERSEY CORP.) 22 March 1983, see abstract & pages 1-8.	1-17
Y	CA, A, 724,623 (DOW CORNING CORPORATION) 28 December 1965, see examples and pages 19-20.	1-17
Y	Choosing The Right Polyglycol, Technical Service and Development (Dow Chem. Company) Midland, Michigan, 3rd Ed. 1959.	1-17
Y	US, A, 3,959,176 (MAHN ET AL.) 25 May 1976, see entire document.	1-17
A	US, A, 4,344,863 (ROBBINS ET AL.) 17 August 1982, see entire document.	1-13
Y	US, A, 4,474,919 (POLATAJKO-LOBOS ET AL.) 02 October 1984, see column 1, line 50 to column 2, line 34.	14-17
<p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step.</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
15 OCTOBER 1990	26 DEC 1990	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 DANIEL S. METZMAIER	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

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V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

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

1. Claim numbers _____, because they relate to subject matter¹ not required to be searched by this Authority, namely:

2. Claim numbers _____, 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 out¹, specifically:

3. Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

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

- I. Claims 1-13, drawn to a defoaming composition, a process of defoaming, and a defoamed liquid.
- II. Claims 14-15, drawn to a method of inhibiting-swelling in a polymer.
- III. Claims 16-17, drawn to a polymer which the swelling has been inhibited.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. 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 claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.