

1

3,215,635

DEFOAMING COMPOSITIONS

Raymond Liebling, Springfield, and Thomas F. Groll, Jr., Elizabeth, N.J., assignors to Nopco Chemical Company, Newark, N.J., a corporation of New Jersey
No Drawing. Filed Aug. 2, 1962, Ser. No. 214,202
13 Claims. (Cl. 252—321)

The present invention relates to anti-foaming or defoaming compositions. More particularly, the present invention relates to new and improved liquid defoaming compositions which are especially adapted to defoam dilute black liquor in papermaking processes.

The soda and kraft or sulfate process for papermaking is commonly referred to as the alkaline pulping process since the chemicals used are essentially sodium hydroxide or caustic in the former and sodium sulfate or salt cake and sodium hydroxide in the latter. This process currently represents one of the most utilized pulping procedures in the pulp and paper industry. One of the reasons for the continued growth of this procedure is that the spent chemicals can be reclaimed and reused, thus giving it an advantage over other methods. However, one of the greatest disadvantages of this process is the troublesome foam which occurs during the pulp screening and washing operations.

The alkaline pulping process is performed by first cooking the wood chips in digesters and then drawing off the spent chemicals for reuse. The resulting pulp fibers are then washed free in brown stock washers of a large amount of residual chemicals. These washers are a series of vats usually three or four in number which alternatively dilute the pulp with water and thicken it by picking it up on large rotary screens. From the brown stock washers, the pulp travels to the screen room where it is again diluted with water and put through vibrating screens which accept the now completely delignified fibers and reject the clumps of unpulped fibers, knots and other foreign material. Foam problems are severe in the screen room since the diluted pulp is subjected to violent agitation by the screens. The water removed from the pulp after the screening operations is referred to as the dilute black liquor and, for the sake of economy, is normally used as the dilution water for the third or fourth stage of the brown stock washers. This dilute black liquor is a foaming material, containing from about 0.001% to 0.1% by weight of solids and has a pH of about 12. The foaming of the dilute black liquor increases with the increase of the resin content of the wood used in this process.

Defoamers are generally used in most alkaline pulp mills during the screening operations so that a more efficient screening is accomplished and to prevent the pulp thickeners, utilized after the screening operations, from becoming clogged with entrapped air. When water dispersible defoamers are used during the screening operation, the control of foam and entrained air in the screening operation contributes to the washing efficiency of the pulp during the alkaline pulping process. This is accomplished by the fact that the screening efficiency of the pulp is increased, allowing ease of flow of the pulp throughout the thickeners and subsequent washers.

Accordingly, it is an object of the present invention to provide for new and improved defoaming and anti-foaming compositions.

Another object of the present invention is to provide for new and improved anti-foaming and/or defoaming compositions which are especially adapted for the defoaming of dilute black liquor.

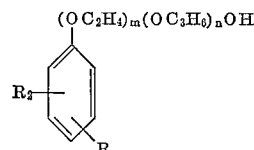
A still further object of this invention is to provide for new and improved anti-foaming and/or defoaming compositions which control foaming during the screening and

2

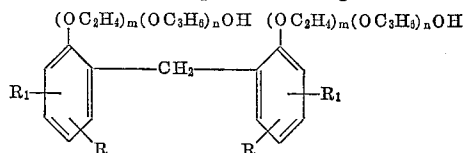
knotting operations as well as in other steps or operations of alkaline pulping processes.

Other objects will become apparent from the detailed description given hereinafter. It is intended, however, that the detailed description and specific examples are not limiting, but merely indicate the preferred embodiments of this invention since various changes and modifications in the scope of the invention will become apparent to those skilled in the art.

In accordance with the present invention we have discovered that compositions which are mixtures or blends of (1) from about 50% to about 89% by weight of an aliphatic or alicyclic or aromatic hydrocarbon or mixtures thereof containing at least 6 carbon atoms, (2) from about 5% to 25% by weight of at least one higher fatty acid having from about 6 to 24 carbon atoms, (3) from about 5% to about 24% by weight of at least one higher fatty alcohol, (4) about 1% to about 20% of a low foaming surfactant, said surfactant being selected from the class consisting of polyoxyalkylated alkyl phenols having the formula:



and polyoxyalkylated bisphenols having the formula:



wherein R is a straight or branched chain, substituted or unsubstituted alkyl substituent having from 1 to 13 carbon atoms such as butyl, nonyl, octyl, isooctyl, hexyl, cyclohexyl, dodecyl, decyl and benzyl radicals; R₁ is selected from the group consisting of H and straight or branched chain substituted or unsubstituted alkyl substituents having from 1 to 13 carbon atoms, such as butyl, methyl, propyl, isopropyl, pentyl, ethyl and hexyl; m is an integer ranging from 4 to 25, preferably 4 to 14, and n is an integer ranging from 1 to 20, preferably 1 to 14, both m and n being subject to the limitations more fully explained hereinafter, and (5) from about 0% to 20% of a lower molecular weight monohydroxy aliphatic alcohol having from one to five carbon atoms wherein the total amount of hydrocarbon or hydrocarbon mixtures and higher fatty acid constitutes at least 75% by weight of the total composition, provide a new and improved defoamer for liquids such as the dilute black liquor produced in the papermaking process.

In the above polyoxyalkylated alkyl phenol and polyoxyalkylated bisphenol formula the symbol n represents an integer ranging from 4 to 25 and m stands for an integer ranging from 1 to 20. The number of ethylene oxide units is determined by the value of m and the number of propylene oxide units is determined by the value of n. Within the definitions of m and n the following relationship must be observed. The value of m must always be at least 0.85 times and at most 1.7 times the value of n. Also the value of m must be at least 0.7 and at most 5.0 times the total number of carbon atoms present in R₁ and R. Therefore, in order to produce a polyoxyalkylated alkyl phenol and polyoxyalkylated bisphenol for use in the defoaming composition of this invention, the number of ethylene oxide groups should be at least approximately equal to the number of propylene oxide groups (no less than 0.85) as well as at least approximately equal to the

total number of carbon atoms in the R_1 and R substituents (no less than 0.7) and in any case no greater than approximately twice the propylene oxide groups and five times the total number of carbon atoms in the R_1 and R substituents. The values of m and n in the above formulas are to be construed in the light of the above discussion.

It is known to utilize emulsifying agents such as polyethylene glycol esters of higher fatty acids in defoaming compositions to disperse or otherwise bring into contact in the solution to be treated, the defoaming materials. However, we have found that when the aforementioned polyoxyalkylated alkyl phenols and bisphenols which are low foam surfactants were substituted for the previously utilized emulsifying agents in a defoaming composition, an unexpected increase in the defoaming activity of the composition occurred, particularly in the case where the liquor to be treated was the dilute black liquor formed during the screening and knotting operations in alkaline pulp mills. On the other hand, we have found that when only a portion of polyethylene glycol ester of the higher fatty acid emulsifying agent is replaced by the polyoxyalkylated alkyl phenol or bisphenol in the defoaming compositions containing besides the polyethylene glycol ester of the higher fatty acid, an aliphatic, alicyclic or aromatic hydrocarbon, or mixtures thereof, a low molecular weight monohydric alcohol, a high molecular weight fatty acid and a high molecular weight fatty alcohol, a six component composition is obtained that is far inferior to even that of utilizing only the polyethylene glycol fatty acid ester in the above composition. Thus, it was unexpected to find that by completely replacing the emulsifying agents such as polyethylene glycol fatty acid esters in a defoamer composition with a low foam surfactant such as polyoxylated alkyl phenol and bisphenol, a far superior defoamer for the dilute black liquors prepared in the alkaline pulping process was produced as compared to other known defoamer compositions.

The polyoxylated alkyl phenols such as those disclosed in U.S. Patent No. 3,021,372, Dupre et al., U.S. Patent No. 2,903,486, Brown et al., as well as the polyoxylated alkyl bisphenols have been previously utilized as low foam surfactants. We have discovered that by incorporating these low foam surfactants as well as other condensates coming within the heretofore described generic formula, into a composition consisting of a low molecular weight aliphatic monohydroxy alcohol, an aliphatic, alicyclic or aromatic liquid hydrocarbon or mixtures thereof, a mixture of higher fatty alcohols and higher fatty acids that a new and improved defoamer is produced which is effective in defoaming dilute black liquors produced during the alkaline pulping process.

The compositions of the present invention contain liquid aliphatic, alicyclic or aromatic hydrocarbons or mixtures thereof as one of the essential components. The liquid aliphatic, alicyclic, aromatic hydrocarbons and mixtures thereof suitable for use in the practice of this invention are liquids at room temperature and atmospheric pressure having a viscosity of from about 30 SUS to about 400 SUS (Saybolt Universal Seconds at 100° F.), a minimum boiling point of at least 150° F. and contain from 6 to 25 carbon atoms. Hydrocarbons such as benzene, hexane, heptane, octane, paraffin oil, mineral seal oil, kerosene, naphtha, naphthenic mineral oil and paraffinic mineral oil, etc. are examples of some of the hydrocarbons which have been found to be fully suitable for use as the liquid hydrocarbon component in the novel composition of this invention. If desired, mixtures of any two or more of these or other similar hydrocarbons can be employed such as the conventional commercial mixtures. In the practice of the invention, the liquid aliphatic, alicyclic or aromatic hydrocarbon component or mixtures thereof comprises from about 50% to 89% by weight of the novel defoaming compositions.

The second component of the novel and improved composition comprises a fatty acid having a carbon chain

length of from about 6 to 24 carbon atoms. Either saturated, unsaturated, or hydroxylated fatty acids coming within the above definition may be employed. Examples of suitable fatty acids which may be utilized as the second component in the novel defoamer of this invention include stearic acid, oleic acid, 12-hydroxy stearic acid, ricinoleic acid, lauric acid, palmitic acid, etc. If desired, mixtures of two or more of these fatty acids may be employed in the fatty acid component of this invention. The fatty acid component may comprise from about 5% to about 25% by weight of the defoaming composition as long as the total weight percentage of the hydrocarbon and the acid is at least 75% by weight of the total composition.

The third component of the novel and improved composition comprise a fatty alcohol or mixtures thereof. The fatty alcohols that are used in this invention are saturated or unsaturated, straight or branched chain alcohols and have from about six to about twenty-two carbon atoms in the chain. Examples of these alcohols include octyl alcohol, iso-octyl alcohol, nonyl alcohol, decyl alcohol, tridecyl alcohol, hexadecyl alcohol, stearyl alcohol, oleyl alcohol, ricinoleyl alcohol and mixtures thereof including common commercial mixtures. In the defoaming compositions, the fatty alcohol component comprises from about 5% to about 24% by weight of the total defoaming composition.

The polyoxyalkylated alkyl phenol component is a condensate of one mole of an alkyl phenol such as nonyl phenol, dodecyl phenol, butyl phenol, octyl phenol, amyl phenol, etc. with from 4 to 25 moles of ethylene oxide and further condensed with from 1 to 20 moles of propylene oxide. The ratio of moles of ethylene oxide to moles of propylene oxide condensed on the phenol molecule should be no less than 0.85 and no greater than 1.5. In all cases the moles of ethylene oxide condensed on the phenol ring should be equal to no less than 0.7 times the total number of carbon atoms in the alkyl substituents of the phenol ring and no more than 5 times the total number of carbon atoms in the alkyl substituents of the phenol ring. The end product of these condensation reactions will contain one free, unetherified terminal hydroxyl group adjacent to a propyl radical. It is necessary in the present compounds that the oxyethylene groups be positioned adjacent to the benzene ring and that the oxypropylene groups be terminally located at the opposite end of the chain from the benzene ring. The desired results can only be obtained by strict adherence to this specific structure. Typical examples of these compounds are disclosed in U.S. Patent No. 2,903,486, Brown et al. and U.S. Patent No. 3,021,372, Dupre et al.

These polyoxyalkylated alkyl phenols which are utilized in this invention may be prepared by reacting an alkylphenol with ethylene oxide at a temperature of from about 130° C. to about 210° C., preferably from about 150° C. to about 180° C. and in the presence of a strong basic catalyst such as sodium, sodium hydroxide, potassium hydroxide, sodium methoxide, and the like. Pressures from atmospheric to about 30 pounds per square inch gauge may be advantageously utilized. Following the ethylene oxide addition, propylene oxide may be added in a similar way and under similar reaction conditions. If desired, the product may be purified by neutralizing the catalyst, steam stripping until residual oxide odors disappear and then by stripping off water preferably under reduced pressure, but such is not necessary.

In formulating our defoaming compositions, from about 1% to about 20% by weight of the polyoxyalkylated alkyl phenol component may be utilized based on the total weight of the defoamer composition. The preferred amount of this component that may be used in this composition is from about 2% to about 15% by weight based on the total weight of the defoamer composition.

In lieu of the polyoxyalkylene alkyl phenols, polyoxyalkylene bisphenols may be utilized. This component is

a condensate of one mole of an alkyl bisphenol prepared from such compounds as nonyl phenol, dodecyl phenol, amyl phenol, octyl phenol, nonyl phenol, octyl o-cresol, etc. with from 4 to 25 moles per hydroxyl group of ethylene oxide and further condensed with from 1 to 20 moles of propylene oxide per hydroxyl group. The ratio of moles of ethylene oxide per mole of hydroxyl to moles of propylene oxide per mole of hydroxyl condensed on the bisphenol ring should be no less than 0.85 and no greater than 1.5. In all cases the moles of ethylene oxide condensed on each of the phenol moieties of the bisphenol molecule should equal no less than 0.7 times the total number of carbon atoms in the alkyl substituents of the phenol moiety and should be no greater than 5 times the carbon atoms in the alkyl substituents on the phenol moiety. The end product of these condensation reactions will contain on each benzene nucleus, one free unetherified terminal hydroxyl group adjacent to a propyl radical. It is necessary in the present compounds that oxyethylene groups be positioned opposite each benzene ring and that the oxypropylene groups be terminally located at opposite ends of the chain from each benzene ring. The aforementioned beneficial defoaming properties can only be attained by strict adherence to this specific structure.

These polyoxyalkylated alkyl bisphenols may be prepared by reacting an alkyl phenol with formaldehyde or para formaldehyde, or trioxane, etc. at temperature of from about 65° C. to 100° C. for a period of from about 2 to 6 hours or more, so as to form the substituted bisphenol. The bisphenol may be thereafter reacted with 4 to 25 moles of ethylene oxide per hydroxyl radical at a temperature of 150° C. to 200° C. and in the presence of a strong basic catalyst such as sodium, sodium hydroxide, potassium hydroxide and the like. Pressures from atmospheric to about 30 lbs. per square inch gauge may be advantageously employed. Following the ethylene oxide addition, propylene oxide may be added in a similar way and utilizing similar reaction conditions. The product can be purified by stripping off water preferably under reduced pressure. If desired, the ethylene oxide adduct may be purified before the propylene oxide is added, but such is not necessary. In formulating our defoaming composition, from about 1% to about 20% by weight of the polyoxyalkylated alkyl bisphenol component may be utilized based on the total weight of the defoamer composition. The preferred amount of this component which is used in this composition may be from 2% to 15% by weight based on the total weight of the defoamer composition.

The fifth component of the novel defoaming composition of the present invention is a lower molecular weight monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms. Thus, alcohols such as isopropanol, pentanol, methyl alcohol, butyl alcohol, ethyl alcohol, may be utilized. If desired, mixtures of any two or more of these alcohols can be employed in the practice of the invention. In the practice of the invention, the low molecular weight alcohol component of the composition comprises from about 0% to 20% by weight of the novel defoaming composition. Hence, it can be seen that, the alcohol component may be omitted from the defoaming composition of this invention without deleteriously affecting the improved defoaming properties of the novel compositions of this invention. However, for best results, it is preferred that at least 1% by weight of this component be present in the defoaming composition of this invention.

Our defoaming compositions are used in alkaline pulp processing in the following manner. For best results, the defoaming composition of this invention is added to the pulp in the screen room. In some cases, the defoaming composition of this invention may be introduced to the brown stock washers generally in the third or fourth stages of these washers which contain the black liquor. The defoaming compositions are used in amounts of from

about 0.01% to about 0.5% by weight based upon the weight of dry fiber present in the washers. Thus by utilizing our defoaming compositions, foaming of the dilute black liquor in the screening and subsequent operation where foaming is severe is practically eliminated.

The defoaming compositions of this invention as shown by the foregoing examples were prepared by mixing the components at approximately room temperature, moderate warming being required to melt solid (at room temperature) fatty alcohols and fatty acids. All parts given are parts by weight. The products were clear free-flowing liquids. The defoaming compositions prepared were evaluated by testing their ability to defoam black liquor obtained from a paper mill having about 16% by weight of solids as received, but which is diluted to about 0.16% by weight solids just prior to the defoam test as hereinafter described.

The apparatus used in evaluating the defoaming compositions of this invention can be described as follows. A beaker of 1000 cc. capacity (tall form) was used. A curved outlet fused onto the base of the beaker was connected with a rubber or plastic hose to a centrifugal pump. The pump was used to continuously cycle the dilute black liquor from the beaker through the pump and back into the beaker. Pumping was carried out at a rate such that the dilute black liquor in the beaker was agitated by the reentering liquid to such an extent that the formation of foam occurred. The rate was approximately two gallons per minute. The circulating dilute black liquor entered the beaker at a point about 2¼ inches above the surface of the liquid in the beaker and struck the surface of the liquid in the beaker at an angle of about 80°.

In carrying out the testing of the defoamer compositions, 5.0 cc. of concentrated black liquor which contained approximately 16% by weight of solids was diluted with 495 cc. of 95° F. tap water and placed in the beaker of the apparatus. This liquid, when quiescent, filled the beaker to a level of about 3¼ inches from the bottom. Then, 1 cc. of a 5% by volume aqueous emulsion of one of the defoamer compositions was added to the beaker containing 500 cc. of the aforesaid dilute black liquor. The dilute black liquor was warmed to approximately 95° F. during the operation of the test. In operation, the pump and stop watch were started simultaneously. As soon as the operation was started the black liquor started to form large, white easily ruptured bubbles on the surface of the black liquor which indicated that defoaming was taking place. The time in seconds for the cessation of large, easily ruptured bubbles and the onset of small permanent bubbles which indicated that defoaming had ceased marked the end point. The time from the start of the pump until the formation of the small permanent bubbles was an indication of the defoaming ability of the defoamer which was being tested. The longer the time the better was the defoaming action of the defoamer. This procedure was repeated with each of the defoaming compositions to be tested. The test was also run on dilute black liquor which contained no defoamer. This test served as the blank.

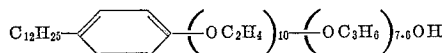
EXAMPLE I

This example is directed to the production of condensates of dodecyl phenol with 10 moles of ethylene oxide and 7.6 moles of propylene oxide.

There was added to a reaction vessel, 575 grams of dodecyl phenol (2.2 moles) and 0.6 gram of KOH. The temperature was raised to about 180° C. in the presence of a nitrogen blanket. 960 grams of (21.8 moles) ethylene oxide were slowly added over a period of about five hours at a temperature of 182° C. to 210° C. during which time all of the 21.8 moles of ethylene oxide reacted. At the end of this period an adduct of phenol and ethylene oxide formed. This adduct was cooled to room temperature. 420 grams of this adduct (0.6 mole) were then placed in a second reaction vessel and heated to about

7

160° C. 264 grams (4.56 moles) of propylene oxide were then added to this adduct over a period of about 6 hours. The temperature of the reaction medium during this period was maintained from about 155° C. to 165° C. During this period 684 grams of an adduct of phenol, ethylene oxide and propylene oxide was produced. This adduct was identified as:



By employing the procedure set forth in Example I except for varying the ring portion of the phenol molecule and the molar ratios of the phenol, ethylene oxide and propylene oxide as shown in Table I below, compounds of one mole of the hydroxy aromatic compound condensed with the substituents and mole proportions shown in Table I were prepared.

Table I

Ring Portion of the Molecule	Moles of Ethylene Oxide	Moles of Propylene Oxide
Nonyl Phenol.....	8.63	6.57
Dinonyl Phenol.....	15.05	12.1
o-Cresol.....	4.55	3.66
o-Cresol.....	5.0	3.0
α-Methyl-benzyl phenol.....	9.6	7.25

EXAMPLE II

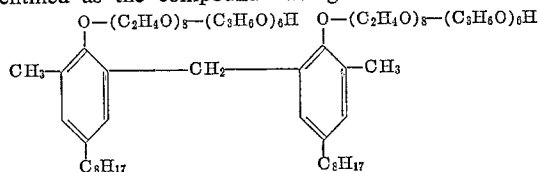
This example illustrates the method of preparing the bisphenol of octyl-o-cresol condensed with 8 moles of ethylene oxide and 6 moles of propylene oxide.

(A) PREPARATION OF OCTYL-O-CRESOL BISPHENOL

7.97 parts of trioxane were added to 91.15 parts by weight of para tertiary octyl-o-cresol and the resulting mixture heated to 55° C. until the phenol was melted. 0.88 part by weight of a 30% by weight concentrated hydrochloric acid solution was carefully added to the mixture of trioxane and phenol and the temperatures allowed to rise to 95° C. and maintained at 95° C. for 6 hours during which time the reaction mass was vigorously agitated. Thereafter the reaction mass which was a pinkish white viscous material was neutralized with 0.96 part by weight of a 50% by weight of an aqueous potassium carbonate solution and agitated for an additional half hour. The mass was then brought up to a temperature of 150° C. while under a nitrogen atmosphere and this temperature was maintained for two hours while the water was stripped from said product. The product which was essentially a bisphenol was pinkish tacky resin having a total alkali content of 0.05%.

(B) PREPARATION OF THE ETHYLENE OXIDE AND PROPYLENE OXIDE CONDENSATE

37.97 parts by weight of ethylene oxide (8 moles/OH) was slowly added to 24.40 parts by weight of the bisphenol of Part A in the presence of 0.03 part by weight of potassium hydroxide as a catalyst. The temperature was maintained at about 185° C. during the ethylene oxide addition. To the resulting condensate was added 37.6 parts by weight of propylene oxide (6 moles/OH). The temperature of the reaction was maintained at about 160° C. during the propylene oxide addition. The product was identified as the compound having the formula:



By employing the procedure set forth in Example II, except for varying the aromatic portion of the bisphenol molecule and the molar proportions of ethylene oxide, propylene oxide and the bisphenol, as shown in Table II below, compounds of one mole of a hydroxy aromatic

8

compound condensed with the substituents and mole proportions shown in Table II were prepared.

Table II

Aromatic Portion of the Molecule	Moles of Ethylene Oxide Per Hydroxyl	Moles of Propylene Oxide Per Hydroxyl
Di-octyl phenylol methane.....	8.68	6.9

EXAMPLE III

This example is directed to a defoamer composition utilizing polyethylene glycol monostearate as the emulsifying agent.

Component:	Weight percent
Mineral oil, naphthenic type hydro refined Esso Coray 40 ¹	70.3
Fatty alcohol, P & G CO 1418 ²	9.0
Tallow fatty acids ³	8.0
Isopropanol	10.0
Polyethylene glycol monostearate 400 (polyethylene glycol monostearate having a molecular weight of about 666)	2.7

¹ A liquid mixture of naphthenic, paraffinic and aromatic hydrocarbons having a viscosity of 100 SUS at 100° F., and a specific gravity of .903.

² A mixture of fatty alcohols containing about 44% of myristyl alcohol, about 24% cetyl alcohol and about 28% stearyl alcohol.

³ A mixture of saturated and unsaturated straight chain monocarboxylic higher fatty acids containing about 43% oleic, about 26% palmitic, about 17% stearic and about 14% other acids.

EXAMPLE IV

This example is directed to incorporating the polyoxy-alkylated alkyl phenol in a defoaming system containing polyethylene glycol monostearate.

Component:	Weight percent
Mineral oil, naphthenic type hydro refined Esso Coray 40	74.2
Tallow fatty acids	8.4
Fatty alcohol, P & G CO 1418	9.5
Polyethylene glycol monostearate 400	2.9
Dodecyl phenol condensed with 10 moles of ethylene oxide and 1.1 moles of propylene oxide	5.0

Examples V through XVIII are directed to the defoaming compositions of this invention.

EXAMPLE V

Component:	Weight percent
Mineral oil, naphthenic type hydro refined Esso Coray 40	78.0
Tallow fatty acids	9.0
Fatty alcohol, P & G TA 1618 ¹	10.0
Bisphenol of octyl-o-cresol condensed with 8 moles of ethylene oxide per hydroxyl and 6 moles of propylene oxide per hydroxyl	3.0

¹ A mixture of aliphatic saturated monohydric fatty alcohols containing 63% stearyl alcohol, 33% cetyl alcohol and 4% myristyl alcohol.

EXAMPLE VI

Component:	Weight percent
Mineral oil, naphthenic type hydro refined Esso Coray 40	78.0
Tallow fatty acids	9.0
Fatty alcohol, P & G TA 1618	10.0
Dodecyl phenol condensed with 10 moles of ethylene oxide and 7.6 moles of propylene oxide	3.0

EXAMPLE VII

Component:	Weight percent
Mineral oil, naphthenic type hydro refined Esso Coray 40	71.7
Tallow fatty acids	8.3

Component—Continued	Weight percent	
Isopropanol -----	8.0	
Fatty alcohol, P & G TA 1618 -----	9.2	
Dodecyl phenol condensed with 10 moles of ethylene oxide and 7.6 moles of propylene oxide -----	2.8	5

EXAMPLE VIII

Component:	Weight percent	
Mineral oil, paraffinic type solvent refined Gulf 333 (a mixture of naphthenic, paraffinic and aromatic hydrocarbons containing 59% of paraffinic hydrocarbons having a viscosity of 100 SUS at 100° F. and a specific gravity of 0.876 at 60° F.) -----	68.8	10
Fatty alcohol, P & G TA 1618 -----	8.8	15
Tallow fatty acids -----	12.0	
Isopropanol -----	7.7	
Dodecyl phenol condensed with 10 moles of ethylene oxide and 7.6 moles of propylene oxide -----	2.7	20

EXAMPLE IX

Component:	Weight percent	
Mineral oil, naphthenic type hydro refined Esso Coray 40 -----	68.8	25
Fatty alcohol, P & G TA 1618 -----	8.8	
Tallow fatty acids -----	12.0	
Isopropanol -----	7.7	
Dinonyl phenol condensed with 15.05 moles of ethylene oxide and 12.1 moles of propylene oxide -----	2.7	30

EXAMPLE X

Component:	Weight percent	
Mineral oil, naphthenic type hydro refined Esso Coray 40 -----	68.8	35
Fatty alcohol, P & G TA 1618 -----	8.8	
Tallow fatty acids -----	12.0	
Isopropanol -----	7.7	
Nonyl phenol condensed with 8.63 moles of ethylene oxide and 6.57 moles of propylene oxide -----	2.7	40

EXAMPLE XI

Component:	Weight percent	
Mineral oil, paraffinic type solvent refined Gulf 333 -----	68.8	45
Fatty alcohol, P & G TA 1618 -----	8.8	
Tallow fatty acids -----	12.0	
Isopropanol -----	7.7	
o-Cresol condensed with 4.55 moles of ethylene oxide and 3.66 moles of propylene oxide --	2.7	50

EXAMPLE XII

Component:	Weight percent	
Mineral oil, paraffinic type solvent refined Gulf 333 -----	68.8	
Tallow fatty acids -----	12.0	55
Fatty alcohol, P & G TA 1618 -----	8.8	
Isopropanol -----	7.7	
Octyl bisphenol condensed with 8.68 moles of ethylene oxide per hydroxyl and 6.9 moles of propylene oxide per hydroxyl -----	2.7	60

EXAMPLE XIII

Component:	Weight percent	
Mineral oil, naphthenic type hydro refined Esso Coray 40 -----	68.8	65
Fatty alcohol, P & G TA 1618 -----	8.8	
Tallow fatty acids -----	12.0	
Isopropanol -----	7.7	
Octyl bisphenol condensed with 8.68 moles of ethylene oxide per hydroxyl and 6.9 moles of propylene oxide per hydroxyl -----	2.7	70

EXAMPLE XIV

Component:	Weight percent	
Mineral oil, paraffinic type solvent refined Gulf 333 -----	68.8	75

Component—Continued	Weight percent
Tallow fatty acids -----	12.0
Fatty alcohol, P & G TA 1618 -----	8.8
Isopropanol -----	7.7
α-Methyl benzyl phenol condensed with 9.6 moles of ethylene oxide and 7.25 moles of propylene oxide -----	2.7

EXAMPLE XV

Component:	Weight percent
Mineral oil, paraffinic type solvent refined Gulf 333 -----	68.8
Tallow fatty acids -----	12.0
Fatty alcohol, P & G TA 1618 -----	8.8
Isopropanol -----	7.7
o-Cresol condensed with 5.0 moles of ethylene oxide and 3.0 moles of propylene oxide ----	2.7

EXAMPLE XVI

Component:	Weight percent
Mineral oil, paraffinic type solvent refined Gulf 333 -----	68.8
Tallow fatty acids -----	12.0
Fatty alcohol, P & G TA 1618 -----	8.8
Isopropanol -----	7.7
Bisphenol of octyl o-cresol condensed with 8 moles of ethylene oxide per hydroxyl and 6 moles of propylene oxide per hydroxyl ----	2.7

EXAMPLE XVII

Component:	Weight percent
Mineral oil, naphthenic type Esso Coray 40 --	85.0
Palm oil fatty acids (48% palmitic acid, 38% oleic acid and 14% other acids) -----	5.0
Fatty alcohol, Adol 52 (90% cetyl alcohol, 6% stearyl alcohol and 4% myristyl) ----	5.0
n-Butanol -----	4.0
Ortho cresol condensed with 4.55 moles of ethylene oxide and 3.66 moles of propylene oxide -----	1.0

EXAMPLE XVIII

In this example, no lower short chain alcohol was used in formulating the defoamer composition.

Component:	Weight percent
Kerosene Esso heating oil (41.4° API density distillation range 325–520° F.) -----	59.0
Behenic acid -----	20.0
Fatty alcohol, Hatcol MC (a mixture of C ₁₄ to C ₁₆ alcohols) -----	9.0
Octyl bisphenol condensed with 8.68 moles of ethylene oxide per hydroxyl and 6.9 moles of propylene oxide per hydroxyl -----	12.0

EXAMPLE XIX

The defoaming compositions of Examples III to XVIII were tested in the manner hereinbefore described for the onset of small permanent bubbles. The results are indicated in the following table.

RESULTS OF THE DEFOAMER TESTS CARRIED OUT ON COMPOSITIONS OF THE PRECEDING EXAMPLES

Composition of Example No.	Time for the onset of small permanent bubbles (seconds)
Blank (no defoamer)-----	3.0
III-----	9.0
IV-----	7.0
V-----	30.0
VI-----	40.0
VII-----	25.0
VIII-----	40.0
IX-----	14.0
X-----	19.0
XI-----	50.0
XII-----	40.0
XIII-----	35.0
XIV-----	50.0
XV-----	37.0
XVI-----	50.0
XVII-----	17.0
XVIII-----	32.0

As seen from the above table the defoamer compositions of this invention as seen in Examples V through XVIII are far superior to those defoamer compositions utilizing polyethylene glycol monostearate (Examples III and IV) either alone or in conjunction with the low foam surfactants utilized in this invention. As shown by the above table, the time required for the objectionable small bubbles to form utilizing the compositions of our invention was in almost all cases in the order of at least twice as great as the time of the formation of small bubbles utilizing polyethylene glycol stearate. Also replacing of part of the polyethylene glycol stearate in the defoaming composition with the polyoxyalkylated alkyl phenol, materially decreased the defoaming ability of the defoamer as seen by a comparison of the defoaming results of Examples III and IV.

EXAMPLE XX

This example is directed to a comparison of a defoaming composition wherein the amount of hydrocarbon and fatty acid components are less than 75% by weight of the total defoaming composition with a defoaming composition prepared according to this invention wherein the amount of hydrocarbon and fatty acid components are at least 75% of the total defoaming composition.

Two defoaming compositions labelled A and B were prepared as follows:

(A)

Component:	Weight percent
Mineral oil, paraffinic type solvent refined	
Gulf 333	50.0
Tallow fatty acids	15.0
Fatty alcohol, P & G TA 1618	10.0
Fatty alcohol, P & G Umbrex ¹	15.0
Isopropanol	5.0
Dodecyl phenol condensed with 10 moles of ethylene oxide and 7.6 moles of propylene oxide	5.0

¹ A liquid mixture of saturated fatty alcohols containing 5% hexanol, 59% octanol, 34% decanol and 2% dodecanol.

(B)

Component:	Weight percent
Mineral oil, paraffinic type solvent refined	
Gulf 333	50.0
Tallow fatty acids	25.0
Fatty alcohol, P & G TA 1618	15.0
Isopropanol	5.0
Dodecyl phenol condensed with 10 moles of ethylene oxide and 7.6 moles of propylene oxide	5.0

The above defoaming compositions were tested in the manner hereinbefore described, for the onset of small permanent bubbles. The results are indicated in the following table.

RESULTS OF THE DEFOAMER TESTS CARRIED OUT ON SAMPLES A AND B OF THIS EXAMPLE

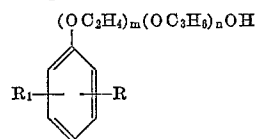
Composition of Sample	Time for the onset of small permanent bubbles (seconds)
A	7
B	45

As shown by Sample A in the above table, the improved defoaming results of this invention are not obtained until the hydrocarbon and fatty acid components of the composition equal at least 75% by weight of the total composition. By just increasing these two components to at least 75% by weight of the total composition, the improved defoaming results are obtained as shown by Sample B.

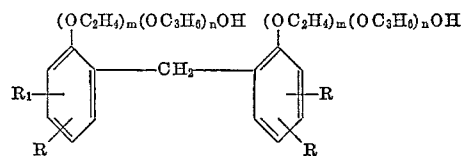
Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A defoaming composition consisting essentially of:

- from about 50% to about 89% by weight of a compound selected from the group consisting of aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons and mixtures thereof, said compound having a boiling point of at least 150° F.,
- from about 5% to about 25% by weight of at least one fatty acid having from about 6 to 24 carbon atoms,
- from about 5% to about 24% by weight of at least one fatty alcohol having from 6 to 22 carbon atoms,
- about 1% to 20% of a compound selected from the class consisting of



and

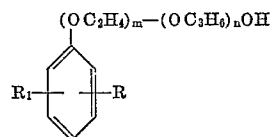


wherein R is a hydrocarbon radical having from 1 to 13 carbon atoms, R₁ is selected from the group consisting of H and alkyl radicals having from 1 to 13 carbon atoms, m is an integer from 4 to 20 and n is an integer from 1 to 20, the ratio m/n is a number from 0.85 to 1.7 and the number of moles of ethylene oxide as represented by m ranges from about 0.7 to 5.0 times the total number of carbon atoms in both of the radicals R₁ and R and

(E) from 0% to 20% of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms, said hydrocarbons and said fatty acid comprising at least 75% by weight of the total defoaming composition.

2. A defoaming composition consisting essentially of:

- from about 50% to about 89% by weight of a compound selected from the group consisting of aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons and mixtures thereof, said compound having a boiling point of at least 150° F.,
- from about 5% to about 25% by weight of at least one fatty acid having from about 6 to 24 carbon atoms,
- from about 5% to about 24% by weight of at least one fatty alcohol having from 6 to 22 carbon atoms,
- about 1% to 20% of a compound having the formula

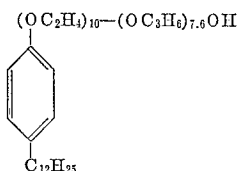


wherein R is a saturated hydrocarbon radical having from 1 to 13 carbon atoms, R₁ is selected from the group consisting of H and a saturated alkyl radical having from 1 to 9 carbon atoms, m is an integer from 4 to 25 and n is an integer from 1 to 20, the ratio of m/n is a number from 0.85 to 1.7 and the number of moles of ethylene oxide as represented by m ranges from about 0.7 to 5.0 times the total number of carbon atoms in both of the radicals R₁ and R and

13

(E) from about 0% to 20% of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms,
said hydrocarbon and said fatty acid comprising at least 75% by weight of the total defoaming composition.

3. A defoaming composition consisting essentially of:
(A) from about 50% to about 89% by weight of a compound selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons and mixtures thereof, said compound having a boiling point of at least 150° F.,
(B) from about 5% to about 25% by weight of at least one fatty acid having from about 6 to 22 carbon atoms,
(C) from about 8% to about 24% by weight of at least one fatty alcohol having from 6 to 24 carbon atoms,
(D) about 1% to 20% of a phenol compound having the formula

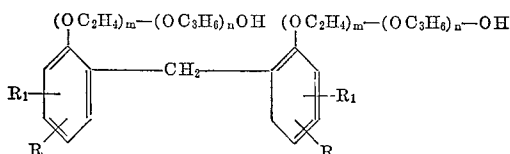


(E) from about 0% to 20% by weight of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms,
said hydrocarbon and said fatty acid comprising at least 75% by weight of the total defoaming composition.

4. The defoaming composition of claim 3 wherein the alcohol is isopropanol.

5. The defoaming composition of claim 3 wherein said phenol compound is present in an amount of about 2 to 3.5% by weight.

6. A defoaming composition consisting essentially of:
(A) from about 50% to about 89% by weight of a compound selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons and mixtures thereof, said compound having a boiling point of at least 150° F.,
(B) from about 5% to about 25% by weight of at least one fatty acid having from about 6 to 24 carbon atoms,
(C) from about 5% to about 24% by weight of at least one fatty alcohol having from 6 to 22 carbon atoms,
(D) from 1 to 20% of a bisphenol compound having the formula:



wherein R is a hydrocarbon radical having from 1 to 13 carbon atoms, R₁ is selected from the group consisting of H and alkyl radicals having from 1 to 13 carbon atoms, m is an integer from 4 to 20 and n is an integer from 1 to 20, the ratio of m/n is a number from 0.85 to 1.7 and the number of moles of ethylene oxide as represented by m ranges from about 0.7 to 5.0 times the total number of carbon atoms in both of the radicals R₁ and R

(E) from about 0% to 20% of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms,
said hydrocarbon and said fatty acid comprising at least 75% by weight of the total defoaming composition.

14

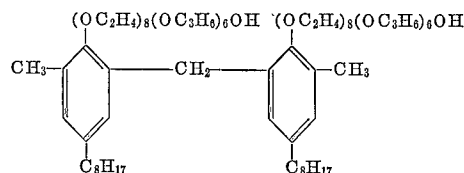
7. The composition of claim 6 wherein R₁ is CH₃—.

8. A defoaming composition consisting essentially of:
(A) from about 50% to about 89% by weight of a compound selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons and mixtures thereof having a boiling point of at least 150° F.,

(B) from about 5% to about 25% by weight of at least one fatty acid having from about 6 to 24 carbon atoms,

(C) from about 8% to 24% by weight of at least one fatty alcohol having from 6 to 22 carbon atoms,

(D) about 1% to 20% of a bisphenol compound having the formula:



(E) from about 0% to 20% by weight of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms,
said hydrocarbon and said fatty acid comprising at least 75% by weight of the total defoaming composition.

9. The defoaming composition of claim 8 wherein said aliphatic alcohol is isopropyl alcohol.

10. The defoaming composition of claim 8 wherein said bisphenol compound is present in said composition in an amount of about 2% to 3.5% by weight.

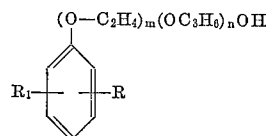
11. In a papermaking process, a method of defoaming the pulp and liquor slurry in the screening and washing operations comprising adding to the pulp about 0.01 to about 0.5% by weight of a defoaming composition consisting essentially of:

(A) from about 50% to about 89% by weight of a compound selected from the group consisting of aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons and mixtures thereof, said compound having a boiling point of at least 150° F.,

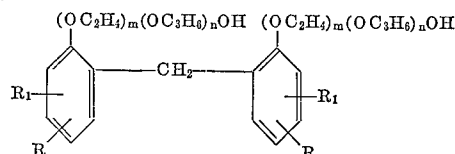
(B) from about 5% to about 25% by weight of at least one fatty acid having from 6 to 24 carbon atoms,

(C) from about 5% to about 24% by weight of at least one fatty alcohol having from 6 to 22 carbon atoms,

(D) about 1% to 20% of a compound selected from the class consisting of



and



wherein R is a hydrocarbon radical having from 1 to 13 carbon atoms, R₁ is selected from the group consisting of H and alkyl radicals having from 1 to 13 carbon atoms, m is an integer from 4 to 20 and n is an integer from 1 to 20, the ratio m/n is a number from 0.85 to 1.7 and the number of moles of ethylene oxide as represented by m ranges from about 0.7 to 5.0 times the total number of carbon atoms in both of the radicals R₁ and R

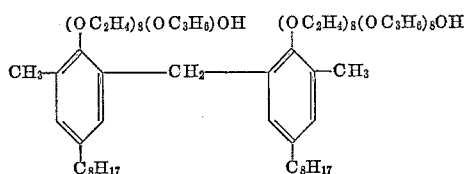
(E) from 0% to 20% of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms,

15

said hydrocarbons and said fatty acid comprising at least 75% by weight of the total defoaming composition.

12. In a papermaking process, a method of defoaming the pulp and liquor slurry in the screening and washing operations comprising adding to the pulp about 0.01 to about 0.5% by weight of a defoaming composition consisting essentially of:

- (A) from about 50% to about 89% by weight of a compound selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons and mixtures thereof having a boiling point of at least 150° F.,
 (B) from about 5% to about 25% by weight of at least one fatty acid having from about 6 to 24 carbon atoms,
 (C) from about 8% to about 24% by weight of at least one fatty alcohol having from 6 to 22 carbon atoms,
 (D) about 1% to 20% of a bisphenol compound having the formula:



- (E) from about 0% to 20% by weight of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms,
 said hydrocarbon and said fatty acid comprising at least 75% by weight of the total defoaming composition.

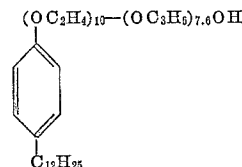
13. In a papermaking process, a method of defoaming the pulp and liquor slurry in the screening and washing operations comprising adding to the pulp about 0.01 to about 0.5% by weight of a defoaming composition consisting essentially of:

- (A) from about 50% to about 89% by weight of a compound selected from the group consisting of

16

aliphatic hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons and mixtures thereof, said compound having a boiling point of at least 150° F.,

- (B) from about 5% to about 25% by weight of at least one fatty acid having from about 6 to 24 carbon atoms,
 (C) from about 8% to about 24% by weight of at least one fatty alcohol having from 6 to 22 carbon atoms,
 (D) about 1% to 20% of a phenol compound having the formula:



- (E) from about 0% to 20% by weight of a saturated monohydroxy aliphatic alcohol having from 1 to 5 carbon atoms,
 said hydrocarbon and said fatty acid comprising at least 75% by weight of the total defoaming composition.

References Cited by the Examiner

UNITED STATES PATENTS

2,797,198	6/57	Chappell	252—358
2,868,734	1/59	De Castro et al.	252—358
2,903,486	9/59	Brown et al.	260—613
3,020,137	2/62	Condo	260—613
3,021,372	2/62	Dupre et al.	260—613
3,064,057	11/62	Liebling et al.	260—613

OTHER REFERENCES

Sill, abstract of application, Serial No. 144,208, published Aug. 5, 1952, 661 O.G. 309—310.

JULIUS GREENWALD, *Primary Examiner*.

ALBERT T. MEYERS, *Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,215,635

November 2, 1965

Raymond Liebling et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 22 to 28, for that portion of the formula reading " $R_2 -$ " read -- $R_1 -$ --; column 4, line 55, for "about"

read -- about --; line 56, for " 180° " read -- 185° --; column 12, lines 25 to 30, for the right-hand portion of the formula reading " $-R$ " read -- $-R_1$ --; column 14, line 44, after "from" insert -- about --; column 15, lines 21 to 28, for the upper left-hand portion of the formula reading " $(OC_2H_4)_8(OC_3H_6)OH$ " read -- $(OC_2H_4)_8(OC_3H_6)_6OH$ --;

same formula, for the upper right-hand portion of the formula reading

" $(OC_2H_4)_8(OC_3H_6)_8OH$ " read -- $(OC_2H_4)_8(OC_3H_6)_6OH$ --.

Signed and sealed this 10th day of September 1968.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,215,635

November 2, 1965

Raymond Liebling et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 22 to 28, for that portion of the formula reading " $R_2 -$ " read -- $R_1 -$ --; column 4, line 55, for "tbout"

read -- about --; line 56, for " 180° " read -- 185° --; column 12, lines 25 to 30, for the right-hand portion of the formula reading " $-R$ " read -- $-R_1$ --; column 14, line 44, after "from" insert -- about --; column 15, lines 21 to 28, for the upper left-hand portion of the formula reading " $(OC_2H_4)_8(OC_3H_6)OH$ " read -- $(OC_2H_4)_8(OC_3H_6)_6OH$ -

same formula, for the upper right-hand portion of the formula reading

" $(OC_2H_4)_8(OC_3H_6)_8OH$ " read -- $(OC_2H_4)_8(OC_3H_6)_6OH$ --.

Signed and sealed this 10th day of September 1968.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents