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(54) **Antifoaming agents**

(57) A silicone-free antifoaming agent comprises a) ethylene bis(stearic amide) or a related compound, b) a paraffin wax, c) hydrophobic silica and d) an oil. The composition may also contain e) one or more emulsifiers, and may also contain f) water. The antifoaming agents are particularly useful in aqueous textile treatment liquors under high temperature conditions.

SPECIFICATION

Antifoaming agents

When many processes are carried out in the presence of water, undesirable foam formation often takes place. Antifoaming agents are used to prevent the formation of foam, to destroy foam which has already formed or for both of these purposes. If silicone-based antifoaming agents are used in processes involving textile goods, particularly under HT conditions, that is, at temperatures above 100°C, spots of silicone oil may appear on the goods. Such spots cannot easily be washed off without damage to the goods, and for this reason it is desirable to use silicone-free antifoaming agents in HT processes. However, although many known silicone-free agents have good antifoaming properties at low temperatures or even at 98-100°C, under HT conditions, particularly those in jet dyeing machines, they are ineffective or insufficiently active.

According to the present invention, there are provided novel silicone-free antifoaming compositions which are particularly active and surprizingly are also effective under HT conditions.

The present invention provides a silicone-free antifoaming agent comprising

a) a compound of formula I

$$R - X - A - X - R \qquad \mathrm{I}$$

in which each R, independently is a saturated or unsaturated aliphatic hydrocarbon group unsubstituted or substituted by one hydroxyl and/or one aryl group, and having from 7 to 30 carbon atoms, including any aryl substituent each X, independently, is a group of formula

$$-COO-,\ -CONH-,\ -OCONH-\ \text{or}\ -NHCONH-$$

and A is an alkylene group having 1 to 20 carbon atoms

b) a paraffin wax

c) hydrophobic silica and

d) a silicone-free, water-immiscible oil, liquid at 20°C and having a boiling point of at least 100°C, components a) and b) being dissolved or dispersed, and component c) dispersed, in component d).

Compounds of formula I are known, and are described for example in *J. Org. Chem. 20* (1955), 695-699 or Chapter 7, Vol. 1 of "Industrial Waxes" by H. Bennett (Chemical Publishing Company Inc., N.Y., 1975).

In the compounds of formula I, the groups X are preferably identical, and more preferably are both –CONH– bonded to A at the N-atom.

Group A is preferably a straight-chain alkylene group of 1-10 carbon atoms, more preferably of 1-6 carbon atoms.

The two groups R are preferably identical and are preferably R' where R' is alkyl or alkenyl with 11 to 27 carbon atoms, optionally substituted with one hydroxy group. More preferably R is R" where R" is alkyl or alkenyl with 13-21 carbon atoms, optionally substituted with one hydroxy group, especially those derived from fatty acids, such that the group R"·CO is myristoyl, palmitoyl, stearoyl, oleoyl, ricinoleoyl or behenoyl, preferably palmitoyl, oleoyl, behenoyl and stearoyl, particularly stearoyl.

Preferred compounds of formula I are those of formula Ia

$$RCONH \left(CH_2 \right)_n NHCOR \qquad \mathrm{Ia}$$

where n = 1-10, more preferably of formula Ia'

$$R'CONH \left(CH_2 \right)_{n'} NHCOR' \qquad \mathrm{Ia'}$$

where both groups R' are identical and n' is 1-6, particularly those of formula Ia"

$$R''CONH \left(CH_2 \right)_{n''} NHCOR'' \qquad \mathrm{Ia''}$$

where both groups R" are identical and n" is 2-6.

The paraffin wax of component b) may be a mineral or synthetic wax consisting predominantly of saturated hydrocarbons and preferably has a melting point of at least 60°C, preferably at least 80°C, more preferably 80-180°C. Preferred mineral waxes include non-oxidized microcrystalline and semi-microcrystalline waxes, hard paraffins (predominantly n-paraffins) obtainable from distillation of crude oil; and ozocerite. Synthetic waxes include those prepared from hydrogenation of carbon monoxide or polymerisation of olefins, preferably non-oxidized Fischer-Tropsch waxes; polyolefin waxes, particularly polyethylene wax, especially that prepared by the Ziegler synthesis. The synthetic waxes are preferably of relatively low molecular weight, having an average MW below 500,000, more preferably $<100,000$, particularly $<20,000$.

The preferred waxes are polyolefin waxes of average MW 1000-20,000 and m.p. ≥ 80°C, particularly polyethylene waxes obtained by Ziegler synthesis and having a m.p. in the range 80-110°C.

The hydrophobic silica of component c) is preferably one obtained by surface treatment of a colloidal silica of large surface-volume ratio. Surface treatments giving rise to hydrophobic properties are well known and include treatment with fatty alcohols, hydrocarbons, silicone oil or other organosilicon compounds, waxes or fatty amines. It is to be noted that surface treatment of component c) with a silicone does not give rise to any free silicone in the composition of the invention and that a composition according to the invention containing silicone-free treated silica is still to be regarded as silicone-free.

The finely-divided silica which is rendered hydrophobic by surface treatment is preferably "fume silica" obtained by pyrolysis; a silicic acid gel dehydrated without loss of structure; or a precipitated silica gel obtained by aqueous chemical reaction.

It preferably has a specific surface area of 50-600 m^2/g, which remains the same after treatment to give hydrophobic properties.

The silicone-free oil of component d) is preferably a natural or synthetic hydrocarbon oil or a vegetable or animal oil, preferably having a flame point of at least 60°C. As for components a), b) and c), component d) may comprise a mixture of materials, and in fact most oils used as component d) will be a more or less complex mixture of different molecular species.

Natural hydrocarbon oils suitable for use as component d) include those obtainable by distillation of crude oil, bitumen and coal, for example: heavy petroleum or naphtha, boiling range 100-180°C (C_{8-10}); kerosene or paraffin, boiling range 180-230°; (C_{11-12}); gasoil, boiling range 230-305°C (C_{13-17}); light lubricating oil, boiling range 305-405°C (C_{18-25}); heavy lubricating oil, boiling range 405-515°C (C_{26-38}); isoparaffins, boiling range 100-250°C; alkyl aromatics, obtained by catalytic reforming of crude oil, boiling range 190-300°C; oil from low temperature coking of lignite or other bituminous material.

Synthetic hydrocarbon oils include those obtained by Fischer-Tropsch synthesis or by cracking or reforming of crude oil, for example Kogasin I, boiling range 160-230°C (C_{10-13}) and Kogasin II, boiling range 230-320°C (C_{14-18}).

Preferably the oil has a boiling point above the temperature at which the antifoaming agent is intended to be used, preferably above 160°C, more preferably above 200°C. Particularly preferred are gasoil, lubricating oil and high-boiling isoparaffins.

Suitable vegetable and animal oils are predominantly fatty acid triglycerides, which are normally complex mixtures of different triglycerides, each of which may be a triester of two or three different fatty acids. The fatty acids which may be present in vegetable and animal oils are well known. They may be saturated or unsaturated, and may be substituted by one hydroxyl group. In component d) of the composition of the present invention, the preferred vegetable and animal oils are those in which at least 40%, preferably at least 70% of the glyceride-forming fatty acids are ethylenically unsaturated fatty acids of at least 18 carbon atoms, particularly oleic, linoleic, linolenic and erucic acids. Particularly preferred are oils in which the ester-forming unsaturated fatty acids are a mixture of monoethylenically unsaturated acids and diethylenically unsaturated acids, e.g. linoleic acid.

Suitable vegetable and animal oils include coconut oil, linseed oil, palm oil, olive oil, castor oil, peanut oil, rape seed oil, sesame oil, cottonseed oil, corn oil, soya oil, saff-flower oil, sunflower oil, wood oil, fish oil, neats foot oil and sperm oil. Of these, the vegetable oils, particularly rape seed oil, are preferred.

Preferably component d) contains a vegetable or animal oil, and more preferably is a mixture of oils d_1) and d_2) where d_1) is a natural hydrocarbon oil and d_2) is a vegetable or animal oil. The oil mixture preferably contains at least 10% of oil d_2), more preferably at least 25%, still more preferably 25-75% of d_2) by weight.

In the absence of added water, the composition according to the invention comprises a continuous phase of component d) in which components a), b) and c) are dissolved or dispersed as finely as possible. Calculated as a percentage of the total weight of components a), b), c), and d), the concentration of each of components a), b) and c), considered separately and independently, is preferably 0.5-15%, more preferably 1-10%, particularly 2-8%. Preferred compositions are those in which the concentration of each of the three components a), b) and c) is in the range 1-10%, more preferably 2-8%.

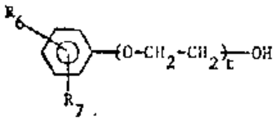
The compositions according to the invention may, in the presence of suitable emulsifiers, be diluted with water to give relatively concentrated stock solutions (or stock dispersions), emulsifier being present in the water used for dilution or, preferably, in the composition itself. The presence of a suitable emulsifier or mixture of emulsifiers (designated as component e) is necessary in order to be able to dilute the composition with water while retaining the fine dispersion of the components and preserving a long shelf life.

The emulsifiers e) may be of the anionic, cationic, non-ionic or amphoteric types, but preferably have HLB (hydrophilic-lipophilic balance) values in the range between 2.5 and 20, or, for Pluronic-type emulsifiers, as low as 1.0. Preferably at least part of the emulsifiers present have HLB values no greater than 12, more preferably no greater than 10. Preferred classes of emulsifiers are as follows:

Anionic:	sulphonated mineral oils and/or mono- or dialkyl benzenes, and salts thereof; sulphated or sulphonated natural oils, fatty acid salts, taurides and phosphoric esters; sulphated non-ionic emulsifiers
Non-ionic:	polyalkylene glycols, especially ethylene oxide (EO)/propylene oxide (PO) copolymers; alkoxylation products of higher fatty alcohols or fatty acid amides; polyethylene glycol esters of long chain fatty acids; polyglycol derivatives in which one OH group is esterified or etherified with a long-chain acyl or alkyl group and the other with a short chain acyl or alkyl group; fatty acid esters of polyfunctional alcohols, e.g. glycerol, mannitol and sorbitol, their cyclic ethers and their polyaddition products with EO and/or PO; hydroxyalkyl fatty acid amides and their alkylene oxide adducts; oxyalkylated mono- and dialkyl phenols
Cationic:	fatty amines; N-alkyl or N-alkenyl mono- or polypropylenepolyamines; condensation products of fatty acids with N-(hydroxyethyl)ethylene diamine, N-alkylpolypropylenepolyamines or polyalkylenepolyamines, including imidazolines, any of which can be reacted with alkylene oxides, or converted into salt forms by reaction with acids.
Amphoteric:	condensation products of fatty acids with polyamines or diethanolamine, optionally ethoxylated and finally sulphomethylated or carboxymethylated; fatty amines or N-alkylpolypropylenepolyamines, optionally ethoxylated and finally sulphomethylated or carboxymethylated; reaction products of primary, secondary or tertiary fatty amines with 2-hydroxy-3-chloropropane sulphonic acid (epichlorohydrin/sodium bisulphite adduct); compounds as described in German Offenlegungschrift 2 807 130.

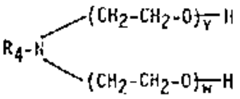
The choice of emulsifier is dependent upon its compatibility with component d) and also with the aqueous system to be used, and can be determined by means of a simple preliminary test. Preferred emulsifiers are those of formulae V-XI, of which V-VIII are nonionic types, IX is anionic, X is amphoteric and XI is cationic:

$$R_4\text{-}(O\text{-}CH_2\text{-}CH_2)_s\text{-}O\text{-}R_5 \qquad (V)$$



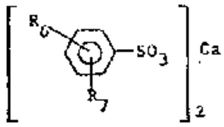
(VI)

$$R_8\text{-}(O\text{-}CH_2\text{-}CH_2)_u\text{-}OH \qquad (VII)$$

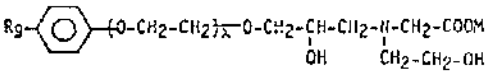


$$R_4\text{-}N\begin{cases}(CH_2\text{-}CH_2\text{-}O)_v\text{-}H\\(CH_2\text{-}CH_2\text{-}O)_w\text{-}H\end{cases}$$

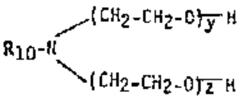
(VIII)



(IX)



(X)



$$R_{10}\text{-}N\begin{cases}(CH_2\text{-}CH_2\text{-}O)_y\text{-}H\\(CH_2\text{-}CH_2\text{-}O)_z\text{-}H\end{cases}$$

(XI)

where

R_4 is the acyl group of a C_{1-18} fatty acid
R_5 is hydrogen or the acyl group of a C_{12-18} fatty acid
R_6 is C_{8-12}alkyl
R_7 is hydrogen or C_{8-12}alkyl
R_8 is a primary or secondary C_{9-18}alkyl or alkenyl group
R_9 is C_{4-12}alkyl
R_{10} is C_{12-18}alkyl or alkenyl
M is hydrogen or a cation, preferably that of an alkali metal
s is 4-10
t is 3-12
u is 2-15
v and w are each at least 1 and v + w is 1-15
x is 8-18 and
y and z are each at least 1 and y + z is 5-20,

whereby the amines of formula X may be present in protonated form. Other preferred emulsifiers are sulphonated mineral oil and the corresponding salts (preferably Na and Ca salts); EO/PO copolymers (Pluronics) of average MW from 1200-2250 and HLB 1.0-15, preferably 2.5-10; and ethoxylation products of sorbitol mono-, di- or tri-esters with acids R_4-OH.

Of the above, the non-ionic type, i.e. those of formulae V-VIII, the Pluronics and the ethoxylated sorbitol esters have the widest range of application. Particularly preferred are the polyalkylene glycol esters of formula V, the Pluronics and the ethoxylated sorbitol esters, especially the esters of formula V.

In order to avoid interference with the antifoaming properties of the active ingredients, the content of emulsifier should be kept as low as possible, consistent with adequate stability of the water-diluted stock dispersion. Preferably the concentration of total emulsifier e), based on a) + b) + c) + d) + e) = 100, is not greater than 30%, more preferably not greater than 20%, particularly 7-20% by weight.

A particularly advantageous embodiment of the invention is one which contains two or more different emulsifiers of different ionic types, in particular, at least one non-ionic emulsifier and at least one anionic emulsifier and particularly when in combination with a particular combination of oils d_1) and d_2).

Accordingly, the invention provides an antifoaming agent containing, in addition to components a), b), c) and d) above,

e_1) at least one non-ionic emulsifier and
e_2) at least one anionic emulsifier,

the weight ratio of e_1):e_2) being greater than 0.5:1 and smaller than 20:1.

Preferred non-ionic emulsifiers e_1) are those described above under e), particularly polyethylene glycol esters of formula (V) having HLB values of 5-12, preferably 6-10. Preferred anionic emulsifiers e_2) are lipophilic emulsifiers (i.e. anionic water-in-oil emulsifiers), preferably sulphonated mineral oil and the corresponding salts (preferably Na and Ca salts). Most preferred products are those having an average molecular weight of at least 460 (calculated as the Na salt).

The weight ratio e_1):e_2) preferably lies between 0.5:1 and 10:1, more preferably between 2:1 and 5:1.

A further preferred embodiment of the invention contains in addition to e_1) and e_2)

e_3) a hydrophilic emulsifier.

The hydrophilic emulsifier e_3) is generally of the type suitable for use as an oil/water emulsifier, and has an HLB value greater than 10, preferably 10.5-20, more preferably 11-18. It may be of any ionic type listed above, but is preferably non-ionic or amphoteric, and more preferably is of formula VI, VII or X, or an ethoxylated sorbitol ester or a Pluronic.

When e_3) is non-ionic, it may be chemically similar to emulsifier e_1), but differs in that e_3) must always have a higher HLB value than e_1), preferably by at least 1 HLB unit. More preferably e_1) has an HLB value $\leqslant 10$ and e_3) has an HLB value $\geqslant 11$.

When e_3) is present, the weight ratio of e_3) to [e_1)+e_2)] is preferably from 0.04:1 to 1.5:1, more preferably from 0.1:1 to 0.4:1. The presence of emulsifier e_3 improves the stability of the product to hard water.

The composition according to the invention may further contain f) water, in an amount preferably less than 80% by weight of the total composition a)+b)+c)+d)+e)+f), more preferably less than 40%. The resulting composition may be a water-in-oil emulsion or an oil-in-water emulsion, depending upon the concentration of water and the concentration and type of emulsifiers present. Such compositions are so-called stock dispersions which may readily be dispersed further in water for use as antifoaming agents in aqueous systems. Preferably, however, component f) is not added, and the compositions contain no significant quantities of water.

The compositions according to the invention are preferably pourable liquids at room temperature, with a rotary viscosity of 5-10,000 cp, preferably 5-5000 cp at room temperature.

The compositions may be prepared by simple mixing together of the components. A preferred sequence of operations is that component a) is dissolved or dispersed in an oil d), component b) is separately dissolved or dispersed in an oil d) which may be the same or different, then both oil solutions or dispersion are mixed together and component c) is added. When two different oils d_1) (mineral oil) and d_2) (vegetable or animal oil) are present, then preferably component a) is dissolved or dispersed in d_2) and component b) in

d_1).

In order to prepare a fine dispersion of a) or b) in oil d), a) or b) is preferably heated with a portion of the oil until a hot solution is obtained, and this is then cooled or is poured into a further portion of the oil, stirred at room temperature. A microcrystalline wax can also be used in the form of 'petrolatum', which is a dispersion of wax in mineral oil.

If an emulsifier is present, this may be added at any stage in the mixing process, but preferably after components a), b) and d) have already been mixed together. When two emulsifiers e_1) and e_2) are present, then these may be added together with c) to the mixture of a), b) and d) or, when two oils d_1) and d_2) are used, it is preferred to mix a solution or dispersin of a) in d_2) with b) in d_1) in the presence of e_1) and adding to the resulting mixture component c) and, optionally after a further addition of d_1), the second emulsifier e_2).

If the composition contains a third emulsifier e_3), this may be added at any stage, but is preferably added after the other emulsifiers are already present.

If the composition contains water f), this is preferably added after all other components a)-e) have been mixed together.

Components a), b) and c) are each known to have anti-foaming properties, but it has been found that used in the compositions of the invention together with d), particularly with a mixture of d_1) and d_2), there is a synergistic effect giving unexpectedly good antifoaming properties, particularly under HT conditions.

The antifoaming compositions of the invention may be added to aqueous systems having a tendency to foam, and in which foam formation has not yet occurred, in order to prevent or inhibit the formation of foam. They may also be added to foam-containing aqueous systems in order to wholly or partially destroy the existing foam and/or to limit or prevent any further foaming.

Aqueous systems having a tendency to foam occur in many technical processes, for example in the preparation of latexes, adhesives, starches, cellulose and sugar; during the work-up of aqueous sludges, particularly in sewage treatment or in the flotation of mineral ores, or of dispersable waste material; during manufacture of paper and nonwoven fabric, particularly in high-speed machines; and in the presence of aqueous systems containing foam-generating components; e.g. polymer dispersions, acrylic resins, leather treatment liquors such as defatting liquors, textile treatment liquors (particularly baths containing dye or optical brightener together with surfactant), and paper coating systems.

The preferred application is foam inhibition in aqueous textile treatment liquors, which may be applied to the goods at any stage of treatment, including sizing, pretreatment, optical brightening, dyeing or printing, crease-resistant finishing and other aftertreatment operations. The term 'textile' is used broadly to cover all stages of manufacture including loose fibres, filaments, threads, yarns, hanks, spools, woven, knitted or tufted fabric, felts, carpets, and semi-finished or fully finished goods. The nature of the textile fibres (natural, synthetic or semi-synthetic) is immaterial.

Such liquors may be applied by any conventional process, e.g. padding, or exhaust at normal or high pressure. The compositions of the invention are particularly suitable for use in textile treatment liquors to be applied under pressure in closed vessels, particularly under HT conditions, that is, at temperatures above 100°C, preferably 102-160°C, more preferably 105-150°C. The compositions are particularly useful in winchbecks and especially in high-speed equipment such as jet dyeing machines, in which there is a high tendency to foam because of steam formation and rapid motion of the goods and liquor, and a tendency for foam to expand when the pressure is released.

The liquors may contain various types of treatment agents e.g. sizes, fibre conditioning agents, desizing agents, detergents, bleaches, wetting agents, resin treatment systems, softening agents, antistatic agents, optical brighteners and dyestuffs; as well as auxiliaries such as carriers, levelling agents and dispersing agents. The compositions of the invention are particularly useful where the aqueous liquor contains treatment agents or auxiliaries which promote foam formation, and bring about an effective reduction in foaming without adversely affecting the treatment of the substrate. Particularly preferred is the use in dyebaths containing disperse dyes, particularly under HT conditions.

The concentration of the composition according to the invention (calculated on the basis of components a), b), c), d) and e) only) in the aqueous system is preferably at least 0.0001 g/l (1 ppm). The optimum concentration for a given system will vary considerably depending on the nature of the system, the process conditions, the particular composition used and the desired effect, but may readily be determined by a simple test. The preferred concentration of the water-free composition in the aqueous system is preferably 0.0001-5 g/l, preferably 0.001-1 g/l; however in paper coating systems it is preferably from 0.0001-0.1 g/kg, more preferably 0.0001-0.01 g/kg.

The following Examples, in which all parts are by weight, and all temperatures are in degrees Centigrade, illustrate the invention.

EXAMPLES 1-12

(i) *Preparation of N'N,-distearoyl ethylenediamine dispersion*

32.2 Parts of N'N-distearoyl ethylenediamine and 128.8 parts of a vegetable or animal oil D_2 (see table) are heated with stirring under vacuum until a clear homogeneous solution is obtained. The resulting solution is added, with stirring and under vacuum (30-60 mbar) to 125.4 parts of the same oil at room temperature. A dispersion is formed, which is cooled to room temperature.

(ii) *Preparation of polyethylene wax dispersion*

22.2 Parts of polyethylene wax B_1 and 222.2 parts of mineral oil D_{11} are heated until a clear solution is obtained. The hot solution is then added to 333.4 parts of the same mineral oil, rapidly stirred at room temperature. A cloudy dispersion is formed.

(iii) *Preparation of final product*

To 286.4 parts of the dispersion product under (i) above is added the product (ii) above, stirring until the mixture is homogeneous. To the homogeneous mixture is then added 106.4 parts of an emulsifier E_{01} and 29.4 parts hydrophobic silica C, and stirring is continued until the silica is fully dispersed. The product (1000 parts) is a fine mobile dispersion with good stability.

(iv) *Identification of starting materials*

Polyethylene wax B_1	molecular weight	2000
	bulk density	220-320 ml/100 g
	m.p.	101±2°
	water content	<0.3%
	specific gravity	0.92
	viscosity at 140°C	180 cp
	hardness (needle penetration 200 g/25 sec./25°C	0.03-0.5

Mineral oil D_{11}	a hydrocarbon mixture with the following specification:	
	b.p. range at normal pressure	320-390°
	specific gravity	0.85-0.95
	water content	0.1%
	acid number	1
	aniline point	70-80
	refractive index n_D^{20}	1.483-1.486
	iodine number	20-30
	flame point	165°

Emulsifier E_{01} A 1:1 molar mixture of: HLB value

$C_{17}H_{33}CO\text{-}(\text{-}OC_2H_4\text{-})_{6.5}\text{-}O\cdot CO\cdot C_{17}H_{33}$	6.5
and $C_{17}H_{33}CO\text{-}(\text{-}OC_2H_4\text{-})_{6.5}\text{-}OH$	10.0

Hydrophobic silica C (Sipernat D_{10}, Degussa, derived from silica hydrogel)

specific surface area (BET)	90 m^2/g
mean particle size	18 nm
bulk density (DIN 53194)	100 g/l
wt. loss on drying (DIN 55921)	3%
wt. loss on ignition (DIN 55921)	7%
pH in 5% dispersion in 1:1 water/methanol (DIN 53200)	8.5
SiO_2 content	98%
Na_2O content	0.8%
SO_3 content	0.8%
retained on sieving (DIN 53580)	0.01%

Table I lists the oil components D_2 which are used in each of Examples 1-12.

Example No.	Oil	constitution
1	D_{21}	peanut oil
2	D_{22}	cottonseed oil
3	D_{23}	fish oil
4	D_{24}	neats foot oil
5	D_{25}	coconut oil
6	D_{26}	flax oil
7	D_{27}	corn oil
8	D_{28}	olive oil
9	D_{20}	castor oil
10	D_{210}	rape seed oil
11	D_{211}	sesame oil
12	D_{212}	sunflower oil

EXAMPLE 13

(i) 61.4 Parts N'N-distearoyl ethylene diamine (A) are heated with 184.2 parts of mineral oil D_{11} while stirring under vacuum until a clear homogeneous solution is formed. The solution is then poured into 184.2 parts of the same oil, stirred at room temperature at 30-60 mbar.

(ii) 33.4 Parts of polyethylene wax B_1 are heated with 333.2 parts of cottonseed oil D_{22} until a clear solution is obtained, and allowed to cool to room temperature with constant stirring. On cooling, a fine dispersion is obtained.

(iii) 429.8 Parts of the dispersion (i), 366.6 parts of the dispersion (ii), 159.4 parts of emulsifier E_{01} and 44.2 parts of hydrophobic silica C are stirred together at room temperature, giving 1000 parts of a homogeneous, fine dispersion.

EXAMPLES 14-18

Example 13 is repeated, using the oils shown in Table II in place of the mineral oil and cottonseed oil.

TABLE II

Example No.	oil mixed with A	oil mixed with B
14	D_{11}	D_{11}
15	D_{210}	D_{22}
16	D_{210}	D_{11}
17	D_{12} (isoparaffin)	D_{22}
18	D_{12}	D_{11}

Isoparaffin D_{12} is a liquid allphatic hydrocarbon with isoparaffin structure, obtained by catalytic synthesis and having the following properties:

boiling range	211-256°
aniline point	88°
aromatic content	0.3%
isoparaffin content	79.9%
n-paraffin content	0.5%
naphthene content	19.3%
sulphur content	2 mg/kg
refractive index n_D^{20}	1.434
viscosity at 25°C	3.1 cSt
flame point	78°

EXAMPLE 19

(i) 33.1 Parts N,N'-distearoyl ethylenediamine are dissolved in 132.2 parts of rape seed oil and added to 128.8 parts of cold rape seed oil, following the procedure of Examples 1-12, (i).

(ii) 22.8 Parts polyethylene wax B_1 are dissolved in 228.3 parts hot mineral oil D_{11} and cooled, following the procedure of Example 13 (ii).

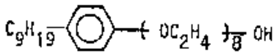
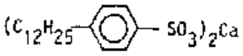
(iii) 294.2 Parts of dispersion (i) and 251.1 parts dispersion (ii) are evacuated to 50 mbar with stirring. Still under vacuum, 82.0 parts of emulsifier E_{01} are added. As soon as the mixture is homogeneous, the vacuum is released and 30.2 parts hydrophobic silica are added. The mixture is again evacuated to 50 mbar and stirred under vacuum until a homogeneous fine dispersion is obtained. The vacuum is again released and a further 342.5 parts of mineral oil D_{11} are added, giving 1000 parts of the final product.

EXAMPLES 20-24

Example 19 is repeated replacing emulsifier E_{01} with the same total weight of the emulsifiers shown in Table III.

TABLE III

Example No.	Single emulsifier type	Non-ionic emulsifier e_1	Anionic emulsifier e_2
20	-	50% E_{11}	50% E_{21}
21	-	50% E_{01}	50% E_{22}
22	E_{02}	-	-
23	E_{22}	-	-
24	E_{21}	-	-

Description of emulsifiers	HLB value
E_{11}: 	12.0
E_{21}: 	8.0
E_{22}: petroleum sulphonate Na salt MW 460-520	<10
E_{02}: Pluronic L 61 (EO/PO block copolymer, MW 1750, 10% wt. EO)	3.0

EXAMPLES 25-30

To 236.5 parts of polyethylene wax dispersion as Example 19 (ii) is added 275.0 parts of the dispersion of Example 19 (i), x parts of emulsifier E_{01} and 28.5 parts hydrophobic silica C. The mixture is evacuated to 70 mbar and stirred intensively until a fine homogeneous dispersion is formed. The vacuum is then released and 318.0 parts mineral oil D_{11}, y parts of emulsifier E_{23} and 28.25 parts hydrophobic silica C are added. The mixture is again evacuated to 70 mbar and stirred vigorously until a fine homogeneous dispersion is obtained.

Table IV shows the values of x and y for each of Examples 25-30

TABLE IV

Example No.	x (parts E_{01})	y (parts E_{23})
25	76.25	37.5
26	106.75	37.5
27	76.25	52.5
28	76.25	22.5
29	106.75	22.5
30	0	0

Emulsifier E_{23} is a sodium petroleum mono-sulphonate with the following properties:

HLB value	<7
average MW	520
emulsifier content	70%
water content	3.2%
oil content	27.3%
inorganic salts	0.4%
density at 15°C	0.980 g/ml
viscosity at 100°C	1000 cSt
flame point	160°

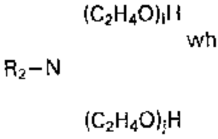
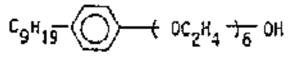
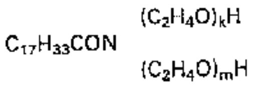
EXAMPLES 31-39

To 100 parts of the product of Example 25 is added 2.0 parts of a further emulsifier e_3 as indicated in Table V.

TABLE V

Example No.	Emulsifier e_3
31	E_{31}
32	E_{21}
33	50% E_{11} + 50% E_{21}
34	E_{33}
35	E_{34}
36	E_{35}
37	E_{36}
38	E_{37}
39	E_{38}

Emulsifiers $E_{31\text{-}38}$ have the following compositions:

	HLB value
E_{31}  $R_2-N\begin{matrix}(C_2H_4O)_iH\\(C_2H_4O)_jH\end{matrix}$ where R_2 = 75% oleyl, 10% stearyl, 15% lauryl-palmityl and $i + j = 10$	11.0
E_{32} as E_{31} but $i + j = 15$	13.0
E_{33} 	11.0
E_{34} product of Example A of USP 4 208 345	16.0
E_{35} Polyoxyethylene 20 - sorbitoltrioleate (Tween 85)	11.0
E_{36} $C_{15}H_{31}(OC_2H_4)_9OH$	13.0
E_{37}  $C_{17}H_{33}CON\begin{matrix}(C_2H_4O)_kH\\(C_2H_4O)_mH\end{matrix}$ $k + m = 10$	13.0
E_{38} $C_{12}H_{25}(OC_2H_4)_5OH$	11.0

EXAMPLE 40

To 100 parts of the product of Example 25 is added 2.0 parts of emulsifier E_{02} (Pluronic L61).

EXAMPLE 41

Example 25 is repeated, but using a polypropylene wax B_2 in place of B_1.

polypropylene wax B_2:	softening point 166°	
	specific gravity	0.86
	MW	14,000
	Brookfield viscosity (spindle 3, 6 rpm, 190°)	3750 cp
	acid No.	0.05

EXAMPLE 42 (Composition containing water (f))

To 100 parts of the product of Example 35 is added 25 parts of demineralized water, and the mixture is stirred at room temperature. A stable milky emulsion is obtained, which could be further diluted with water without forming separate oil and water layers.

APPLICATION EXAMPLE A

Prewashed polyester fabric (Dacron T 54-5-761) is dyed in a jet dyeing machine of volume 1200 ml with 600 ml of an aqueous dye liquor of the following composition:

5% (based on wt. of substrate) C.I. Disperse Red 167
1 g/l levelling agent (C_{16-18} fatty alcohol condensed with 30 moles EO, iodine number = 55)
1 g/l dispersing agent (Turkey red oil)
2 g/l ammonium sulphate
formic acid to pH 5
0.65 g/l composition of Example 1.

The goods:liquor ratio is 1:20 and the liquor circulation rate is 1.5 l/min. The liquor is heated from 30 to 130° over 30 minutes, at 80° the apparatus is closed and pressurized with air to 1 atm. excess pressure. On reaching 130°, dyeing is continued at this temperature for 60 min., then the liquor is cooled and the pressure is released when the temperature has fallen to 85°. Significantly less foam is produced than in the absence of the composition of Example 1. The compositions of Examples 2-12 may be used in the same way.

APPLICATION EXAMPLE B

Application Example A is repeated with the following differences. The liquor contains 0.5 g/l levelling agent, no dispersing agent, and 0.65 g/l of the product of Example 13. The goods:liquor ratio is 1:25 and the circulation rate 1.9 g/l. The bath is heated from 30° to 130° over 50 min. and held at 130° for 30 minutes before cooling. Significantly less foam is produced than in the absence of the composition of Example 13. The composition of Examples 19-23 may be used in the same way.

APPLICATION EXAMPLE C

Cotton cretonne is dyed in the same jet dyeing machine as in Example A, using the following dye liquor (600 ml)

10% (based on substrate) C.I. Reactive Blue 116
60 g/l Glauber's salt
20 g/l soda
0.75 g/l composition of Example 19

at a goods/liquor ratio of 1:20 and circulation rate of 1.5 1/min. The liquor is heated from 30 to 60° over 30 minutes, held at 60° for 60 minutes then cooled to 40°. The amount of foam produced is significantly less than in the absence of the composition of Example 19.

APPLICATION EXAMPLE D

Wool gaberdine is dyed in the apparatus used in Example A with 600 ml of the following liquor:

1.0 % (based on substrate) C.I. Acid Black 52
0.5 g/l levelling agent of Example A
10.0 % (based on substrate) conc. sulphuric acid and
0.5 g/l composition of Example 19

at a goods/liquor ratio of 1:20 and circulation rate of 1.5 l/min. The liquor is heated from 30 to 98° over 30 minutes, held at 98° for 60 minutes, then cooled to 40°. Foam formation is significantly less than when the composition of Example 19 is omitted.

APPLICATION EXAMPLE E

A paper coating paste is made up of the following composition:

26.73 % kaolin
0.05 % sodium tripolyphosphate
0.01 % sodium polyacrylate
0.03 % caustic soda
5.35 % Dow-Latex 620
67.83 % water

and 0.02 % composition of Example 19 (based on the weight of kaolin) is added. The product is tested on the apparatus described in "Wochenblatt für Papierfabrikation", *104*, 117-8 (1976), No. 3 (H. Pummer). Foam formation in the coating paste is considerably reduced by the presence of the composition of Example 19.

APPLICATION EXAMPLE F

Polyester fabric is dyed under HT conditions in a Gaston Country Mini-Jet machine of capacity 650 l (30 kg substrate), using a dye liquor with a particularly high tendency to foam formation.

Substrate: polyester, prewashed and prefixed, 17 kg = 260 m
Dye liquor: 450 l demineralized water containing
0.95 % (based on substrate) C.I. Disperse Red 167
1 g/l levelling agent of Example A
1 g/l dispersing agent of Example A
2 g/l ammonium sulphate
200 ml formic acid (to pH 5)
0.65 g/l product of Example 19

Goods: liquor ratio 1:26, goods velocity 75 m/min. Heated 60-126° over 2 hours, kept at 126° 30 minutes, cooled 126°-60° over 30 minutes. No foam formation was observed over the entire process. Inspection of the dyed goods showed no spots or uneven areas due to the antifoaming agent.

APPLICATION EXAMPLE G

Polyester piece goods are dyed in a Then-Softlow-Jet machine under HT conditions.

Substrate: smooth round-knitted Tergal goods, 130 g/m^2, 110 dtex, 30z15, 9.1 kg.

The machine is filled with cold tap water, 5°dH, liquor to goods ratio 1:15. While heating to 50°, the following additions are made in the given order:

0.2 g/l product of Example 24
2.0 g/l monosodium phosphate
1.4 g/l of the product of Example 14 of USP 4 186 119
1.0 g/l Turkey red oil.

On reaching 50°, 0.05% C.I. Disperse Orange 30 is added and the pH adjusted to 5.2 with acetic acid. The temperature is raised at 1°/min to 90° and 4°/min to 130° and kept at 130° for 30 minutes before cooling to 50°, discharging the spent liquor and giving one cold rinse.

No foam formation could be observed during the dyeing process.

The products of Examples 25-28, 34, 35, 36, 39 and 42 may also be used in the processes of Application Examples A-G.

CLAIMS

1. A silicone-free antifoaming agent comprising
a) a compound of formula I

$$R-X-A-X-R \qquad \text{I}$$

in which each R, independently, is a saturated or unsaturated aliphatic hydrocarbon group unsubstituted or substituted by one hydroxyl and/or one aryl group, and having from 7 to 30 carbon atoms, including any aryl substituent

each X, independently, is a group of formula

$$-COO-, -CONH-, -OCONH- \text{ or } -NHCONH-$$

and A is an alkylene group having 1 to 20 carbon atoms
b) a paraffin wax
c) hydrophobic silica and
d) a silicone-free, water-immiscible oil, liquid at 20°C and having a boiling point of at least 100°C,

components a) and b) being dissolved or dispersed, and component c) dispersed, in component d).

2. An antifoaming agent as claimed in Claim 1 in which component a) is of formula I_a''

$$R''CONH\!-\!(CH_2)_{n''}\!-\!NHCOR'' \qquad I_a''$$

in which both groups R″ are identical and are alkyl or alkenyl with 11-27 carbon atoms, optionally substituted by one hydroxyl group, and n'' is 2-6.

3. An antifoaming agent as claimed in Claim 2 in which component a) is N,N′-distearoyl ethylene diamine.

4. An antifoaming agent as claimed in any one of the preceding claims in which component b) is a polyolefin wax of average molecular weight 1000-20,000 and mp⩾80°C.

5. An antifoaming agent as claimed in any one of the preceding claims in which component d) is a mixture of oils d_1) and d_2) where d_1) is a natural hydrocarbon oil and d_2) is a vegetable or animal oil.

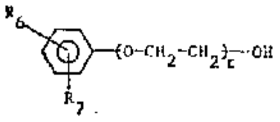
6. An antifoaming agent as claimed in Claim 5 in which component d_2) is a vegetable or animal oil in which at least 40% of the glyceride-forming fatty acids are ethylenically unsaturated fatty acids of at least 18 carbon atoms.

7. An antifoaming agent as claimed in any one of the preceding claims in which the concentration of each of components a), b) and c) is in the range 1-10% of the total weight of components a), b), c), and d).

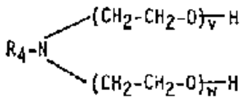
8. An antifoaming agent as claimed in any one of the preceding claims containing, in addition to components a), b), c) and d), an emulsifier or mixture of emulsifiers e).

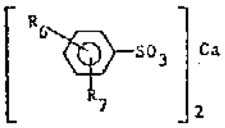
9. An antifoaming agent as claimed in Claim 8 in which the emulsifier or mixture of emulsifiers e) is selected from sulphonated mineral oil, in the form of sodium or calcium sulphonates; ethylene oxide/propylene oxide copolymers of average MW from 1200-2250 and HLB 1.0-15. ethoxylation products of sorbitol mono-, di- or tri-esters with C_{12-18} fatty acids; and compounds of formulae V-XI:

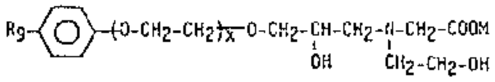
$$R_4\!-\!(O\!-\!CH_2\!-\!CH_2)_s\!-\!O\!-\!R_5 \qquad (V)$$

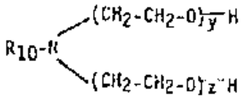

(VI)

$$R_8\!-\!(O\!-\!CH_2\!-\!CH_2)_u\!-\!OH \qquad (VII)$$


$$R_4\!-\!N\begin{matrix}\nearrow (CH_2\!-\!CH_2\!-\!O)_v\!-\!H\\ \searrow (CH_2\!-\!CH_2\!-\!O)_w\!-\!H\end{matrix}$$
(VIII)


(IX)


(X)


$$R_{10}\!-\!N\begin{matrix}\nearrow (CH_2\!-\!CH_2\!-\!O)_y\!-\!H\\ \searrow (CH_2\!-\!CH_2\!-\!O)_z\!-\!H\end{matrix}$$
(XI)

where

R_4 is the acyl group of a C_{12-18} fatty acid

R_5 is hydrogen or the acyl group of a C_{12-18} fatty acid

R_6 is C_{8-12}alkyl

R_7 is hydrogen or C_{8-12}alkyl

R_8 is a primary or secondary C_{9-18}alkyl or alkanyl group

R_9 is C_{4-12}alkyl

R_{10} is C_{12-18}alkyl or alkenyl

M is hydrogen or a cation, preferably that of an alkali metal

s is 4-10

t is 3-12

u is 2-15

v and w are each at least 1 and v + w is 1-15

x is 8-18 and

y and z are each at least 1 and y + z is 5-20,

whereby the amines of formula X may be present in protonated form.

10. An antifoaming agent as claimed in Claim 8 or Claim 9 in which the emulsifier 3) is a mixture of

e_1) at least one non-ionic emulsifier and

e_2) at least one anionic emulsifier

the weight ratio of e_1):e_2) being greater than 0.5:1 and smaller than 20:1.

11. An antifoaming agent as claimed in Claim 10 in which e_1) is a polyethylene glycol ester of formula V, stated in Claim 9, having an HLB value in the range 5-12.

12. An antifoaming agent as claimed in Claim 10 or Claim 11 in which e_2) is a sulphonated mineral oil or a salt thereof.

13. An antifoaming agent as claimed in any one of Claims 10-12 containing, in addition to e_1) and e_2)

e_3) a hydrophilic emulsifier

having an HLB value which is greater than 10 and which is higher than the HLB value of component e_1).

14. An antifoaming agent as claimed in Claim 13 in which component e_1) has an HLB value no greater than 10 and component e_3) has an HLB value of at least 11.

15. An antifoaming agent as claimed in any one of Claims 8-14, containing, in addition to components a), b), c), d) and e), f) water.

16. An antifoaming agent as claimed in Claim 1, as described in any one of Examples 1-42.

17. A process for the preparation of an antifoaming agent as claimed in any one of the preceding claims, comprising the step of mixing together a solution or dispersion of a) in d), a solution or dispersion of b) in d), and c).

18. A process as claimed in Claim 17 for the preparation of an antifoaming agent containing components a), b), c), d_1) d_2) e_1) and e_2), comprising the steps of

i) mixing a solution or dispersion of a) in d_2) with a solution or dispersion of b) in d_1) in the presence of e_1)

ii) adding to the resulting mixture c) and e_2).

19. A process for the reduction of foaming in aqueous systems, characterised by the addition of an effective amount of an antifoaming agent as claimed in any one of Claims 1-16 to the aqueous system.

20. A process as claimed in Claim 19 in which the aqueous system is a textile treatment liquor.

21. A process for textile treatment under HT conditions, characterised in that an effective amount of antifoaming agent as claimed in any one of Claims 1-16 is added to the treatment liquor.

22. A textile treatment liquor containing 0.0001-5 g/l of an antifoaming agent as claimed in any one of Claims 1-16, calculated on the basis of components a), b), c), d) and e) only.

23. A dyebath containing a disperse dye and from 0.001-1 g/l of an antifoaming agent as claimed in any one of Claims 1-16, calculated on the basis of components a), b), c), d) and e) only.

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