

1

3,433,574

DYE LEVELLER CONTAINING AN ANIONIC OR NON-IONIC DETERGENT WITH A FOAM DEPRESSANT MIXTURE OF AN ALKYL ESTER OF AN ALKANOIC ACID, AN ALKYL PHOSPHATE, AND A FATTY ACID OR SOAP

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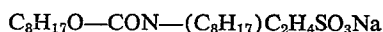
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4 Claims

ABSTRACT OF THE DISCLOSURE

The invention depresses foaming of non-ionic and anionic detergents in a reactive dye or vat dye bath by adding .05 to 4 parts of an alkyl ester of an alkanolic acid wherein at least one of the alkyl radicals of the ester shows at least one ramification of 1 to 4 carbon atoms, .05 to 2 parts of a 4-8 carbon alkyl phosphate, .05 to 1 part of a fatty acid or soap per 10 parts of the non-ionic and/or anionic detergent. Ethylene and/or propylene oxide condensates of fatty alcohols and 4-9 carbon alkyl substituted phenol, fatty alcohol sulfates, sulfonate condensation products of fatty acids with taurines and hydroxyethane sulfonic acid including urethane sulfonates, and other alkyl and aryl sulfonates. An example of the detergent of suppressed foaming tendencies shows a mixture of 5.7% condensate of 8 moles of ethylene oxide and iso-tri-decyl alcohol, 2.8%



16.8% sodium salt of hexa-decylsulfonic acid, 1.7% stearic acid, .8% NaOH (33% strength), 1% tri-isobutyl phosphate, .5% sodium hexametaphosphate, 6.7 2-ethyl-caproic-2 ethyl butyl ester and 64% H₂O. 20 parts per liter or a vat dye, C.I. No. 71,000, were mixed with 10 parts per liter of the above detergent mixture, padded on tent cloth, dried and vatted.

Due to their superior wetting power and their cheapness alkylarylsulfonates and, in particular, alkylsulfonates are frequently preferred in practice to other types of surface-active wetting agents. However, their high foaming power has proved a considerable disadvantage. As is known, the foaming action of the sulfonates can be reduced by addition of soaps. The same applies to reducing the foam formation of oxethylates or fatty alcohols and alkylphenols, which likewise show a remarkable wetting power. Moreover, it is known to prepare detergents with reduced foam formation from anion-active sulfates and sulfonates, soaps and non-ionogenic oxethylates of hydroxyl compounds having 12 to 22 carbon atoms. It has also been suggested to prepare detergent mixtures with reduced foam formation from anion-active sulfates or sulfonates, soaps and oxethylates or alkylphenols having a straight-chain or branched alkyl group of 6 to 12 carbon atoms and a high content of polyphosphates.

However, when using these detergent combinations of two or three substances in practice for textiles and yarns, the decomposition of foam obtained does not meet the increased requirements of wetting power and foam destruction, which are of particular importance in continuous dyeing processes because of the difficulties arising, especially when operating in a caustic alkaline medium.

2

Now, we have found that as wetting agent showing a levelling action and reduced formation of foam, there may be used with particular advantage a mixture containing the following components:

(a) Branched aliphatic carboxylic acid esters of the Formula I



wherein R₁ and R₂ are the same or different saturated or unsaturated alkyl radicals having 4 to 18 carbon atoms, one of the radicals or, preferably, both of them showing one or several, preferably up to 3, ramifications of 1 to 4 carbon atoms,

(b) Phosphoric acid esters of aliphatic alcohols of medium molecular weight which may be partially saponified,

(c) Small amounts of fatty acids or soaps, and

(d) As wetting agents high-molecular oxalkylates of aliphatic or aliphatic-aromatic hydroxyl compounds and/or salts of alkylsulfuric acid esters and/or salts of aliphatic or aliphatic-aromatic sulfonic acids. With regard to the foam reducing action the portion of components (a), (b) and (c) in the mixture and their relation to the wetting substance (component (d)) are of considerable importance. It is, therefore, expedient to use about 0.5 to 4 parts by weight of component (a), 0.05 to 2 parts by weight of component (b), and 0.05 to 1 part by weight of component (c) per 10 parts by weight of the wetting substance (component (d)). Generally the portion of branched carboxylic acid ester of Formula I (component (a) in the mixture amounts to about 4 to 30%, the portion of phosphoric acid esters (component (b)) to about 0.1-20%, that of fatty acids or soaps (component (c)) to about 0.1-10% and that of wetting agents (component (d)) to about 60-95%, referred to the weight of the dry mixture.

The mixtures according to the invention offer the particular advantage that on fibrous materials, in an acid, a neutral and, particularly, in a caustic alkaline medium, the decomposition of foam takes place much more rapidly without impairing the wetting effect, and that at the same time a good levelling action is achieved. It may be considered a further advantage that, when using the mixture according to the invention, the rapid decomposition of foam takes place very uniformly and steadily during the whole wetting or dyeing process.

Due to the foam reducing combination according to the invention it is now possible to use for the wetting baths sulfonates having a high wetting power, but usually also strongly foaming high-molecular sulfonates, oxalkylates, as well as wetting-active urethane sulfonates. These sulfonates may be used in considerably smaller amounts than the low-molecular sulfonates having a weak wetting action which have been used up to now.

Due to its surprisingly good levelling action the combination according to the invention is advantageously used for dyeing and printing textiles.

The mixtures according to the invention may, therefore, be added with particular advantage to dyebaths, padding liquors and printing pastes, or may be used for the preliminary treatment of textiles to be dyed. In this respect the new mixtures are superior to the known combinations of wetting agents which require subsequent addition of phosphoric acid esters or polysiloxanes to the dyebath or printing paste. This subsequent addition has the disadvantage of causing an uneven distribution of the foam reducing agent, frequently accompanied by the formation of foam stains on the dyeings. Moreover, the absorption of the subsequently added foam reducing agents by the fabric is not controllable and may thus lead to uneven dyeings and prints. Furthermore, the consumption

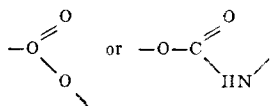
of foam reducing agents must be watched constantly and, if necessary, further amounts must be added. These inconveniences are eliminated when using the mixtures according to the invention which are distinguished by a levelling action.

When dyeing yarns, for example a cotton yarn, on the hank dyeing machine the combinations according to the invention offer another surprising advantage in that they prevent the yarns from floating at the surface of the dye-bath. The known disadvantage of this undesired floating, i.e., the uneven dyeing of the upper portions of the floating yarn, is thus avoided, too. The same applies to the dyeing of piece goods in the winch vat where up to now the floating of the goods caused uneven wetting with the dyestuff and thus uneven dyeings, and even entanglement of the fabric webs. In order to prevent the yarns from floating at the surface of the bath it is advantageous to add to the dyebaths mixtures according to the invention containing as wetting agents oxalkylates and sulfonates. In the preliminary wetting of cross-wound bobbins of dry cotton yarn the combination according to the invention shows a particularly rapid wetting-through activity, which can be seen from the rapid and foamless replacement of the air contained in the yarn by the wetting liquor.

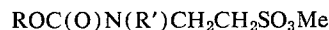
In the wetting baths or dyebaths the mixtures according to the invention are generally used in concentrations from about 0.2 to about 10 grams per liter.

As known high-molecular oxalkylates (component (d)) for the mixtures according to the invention there may be used, for example, products which are prepared on a large scale in industry by addition of about 6 to about 30 mols of ethylene oxide and/or propylene oxide to aliphatic alcohols having from about 8 to about 18 carbon atoms, for example fatty alcohols of natural origin or oxo-alcohols. Moreover, there may also be used the corresponding oxethylates of aliphatic-aromatic hydroxyl compounds such, for example, as alkylphenols having one or several, in particular branched, alkyl radicals of about 4 to 9 carbon atoms. Suitable high-molecular oxalkylates, are for example: p-nonylphenol-nonaethylene-glycol ether, tri-isobutylphenol-octadecaethylene-glycol ether, dodecyl alcohol deca-ethylene-glycol ether, p-nonylphenol-eicosane-ethylene ether, tri-isobutylphenol-triacontane-ethylene-glycol ether, oxo-tridecyl alcohol octaethylene-glycol ether. It is advantageous to use combinations of oxethylates of aliphatic and aliphatic-aromatic compounds, especially the mixture of tridecyl alcohol octaethylene-glycol ether, and 2,4,6-tri-isobutylphenol-triacontane-ethylene-glycol ether. There may also be used the known fatty acid polyglycol esters. Furthermore, the oxalkyl ether chains may, to a certain extent, carry methyl or ethyl side-chains formed by the partial replacement of ethylene oxide by propylene and/or butylene oxide. As high-molecular oxalkylates are generally suitable those which in a 1% aqueous solution show turbidity points of at least 30° C.

As salts of alkylsulfuric acid esters (component (d)) there may be used the alkali metals salts of sulfuric acid esters of aliphatic alcohols having from about 8 to 18 carbon atoms, such, for example, as sulfuric acid esters of fatty alcohols of natural origin or oxo-alcohols. The sulfonates which may be used as component (d) are, on the one hand, the known aliphatic sulfonates containing from about 10 to about 20 carbon atoms and either a sulfonic acid group in terminal or in central position or a statistically distributed sulfonic acid group and wherein the carbon chain may be interrupted by groups of heteroatoms such, for example, as —CONH—,



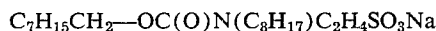
Suitable for use in the process of this invention are, for example, the known petroleum sulfonates, the sulfonates obtained by sulfochlorination or sulfoxidation of benzines or diesel oils, the condensation products of fatty acids with taurines or hydroxyethane-sulfonic acid, in particular urethane-sulfonates of the formula



which are described, for example, in German Patent 1,097,431, or likewise urethanes having shorter alkyl radicals.

On the other hand, there may also be used alkylaryl-sulfonates, in particular the alkali metal salts of the known alkyl-benzenes, e.g., n-dodecylphenyl-sulfonate, tetrapropylene-benzene-sulfonate and sulfonates of alkylbenzene mixtures obtained, for example, by condensation of monochlorinated C₁₀–C₁₄-hydrocarbon mixtures with benzene. Moreover, known benzene-sulfonic acids containing alkyl or alkylaryl radicals linked by means of heteroatoms, such as N,N-dibenzylaniline-4-sulfonic acid, or alkyl-naphthalene-sulfonic acids, such as dibutyl-naphthalene-sulfonic acid, may be used in addition.

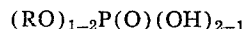
A particularly suitable wetting agent (component (d)) is the combination of the urethane sulfonates described in German Patent 1,097,431, with alkylsulfonates such, for example, as the combination of



with C₁₆H₃₃SO₃Na. Instead of the alkali metal salts of the sulfonates mentioned there may also be used other water-soluble salts, such as ammonium or triethanolamine salts. A combination of oxalkylates and sulfonates has likewise proved every favorable. It is prepared by using preferably 2 to 4 parts by weight of a sulfonate per 1 part by weight of an oxalkylate.

As fatty acids (component (c)) there may be used in the first place carboxylic acids having from about 12 to 18 carbon atoms. As examples of such acids there may be mentioned the following: lauric acid, oleic acid, palmitic acid, behenic acid, resin acids and, in particular, stearic acid, which in the majority of cases are used in the form of salts, for instance in the form of alkali metal or ammonium salts. It is also possible to use other salts of fatty acids or to prepare them in situ, for example, the salts of alkaline earth metals. Mixtures of fatty acid salts may likewise be used. The portion of fatty acids or soaps (component (c)) in the mixture according to the invention amounts generally to about 0.1–5% by weight.

As phosphoric acid esters (component (b)) there are preferred the phosphoric acid esters of alcohols of medium molecular weight having from about 4 to about 8 carbon atoms, for example, tri-isobutyl-phosphate, trioctyl-phosphate and, in particular, tributyl-phosphate. Surprisingly enough, a small addition of phosphoric acid ester suffices to increase the wetting power. It is advantageous to start from partially saponified esters or to saponify the esters partially when preparing the combination according to the invention, i.e., to use them in the form of the salts of phosphoric acid esters of the formula



Suitable carboxylic acid esters of Formula I



(component (a)) are those which contain as radicals R₁ and R₂ saturated or unsaturated alkyl groups containing 4 to 18, preferably 6 to 12 carbon atoms each, of which at least one, preferably both, contain at least one side-chain carrying 1 to 4 carbon atoms, preferably in 2-position.

As examples of said carboxylic acid esters there may be mentioned: 2-ethyl-caproic acid ester of isobutyl alcohol, of 2-ethyl-butanol, of 2-ethylhexanol or of 2,6-dimethyl-heptanol-2; dimethyl-isopropyl-acetic acid ester of 2,6,8-trimethyl-nonanol-4; isodecyclic acid ester of 2-methyl-7-ethyl-undecanol-4, and the ester of tridecyl alcohol ob-

5

tained by oxo-synthesis with 2-methylheptane-carboxylic acid. These esters offer the remarkable advantage that they are stable in caustic alkaline baths because of their poor saponifiability and that they maintain their good foam reducing action. Of particular advantage are the esters of 2-ethylcapronic acid with branched alcohols containing 6 to 8 carbon atoms.

The esters of Formula I can be prepared by known methods which are described, for instance, by Houben-Weyl "Methoden der Organischen Chemie," O. Thieme-Verlag, Stuttgart, 4th edition, vol. 8, p. 508 ff.

The individual components of the mixture are mixed, advantageously in the heat, in the form of thickly liquid, aqueous pastes or solutions having a water content of, for instance, 30 to 80% by weight.

Furthermore, it has proved favorable to add to the mixtures 0.2 to 2% of commercially available inorganic polyphosphates and/or metaphosphates such, for example, as sodium hexametaphosphate. By an addition of this kind the stability of the mixtures in stock solutions (e.g., concentrations of 10 to 20%) as well as to hard water is increased.

In order to improve the consistency and solubility of the pastes there may be added, if necessary, the homogenizers, dispersing agents, solvents and extenders commonly used in the detergents, cleansing agents and textile auxiliaries industries, for example, polyvinyl alcohol, polyglycol ether of medium or high-molecular weight, methyl- or carboxymethyl-cellulose, dinaphthylmethane-disulfonate, aliphatic alcohols, urea, formamide, neutral salts such as sodium sulfate and likewise other emulsifiers and wetting agents such, for instance, as Turkey red oils and fatty amine oxethylates, in minor amounts of about 0.1 to 5% by weight each.

The following examples illustrate the invention but they are not intended to limit it thereto, the percentages being by weight unless otherwise stated.

EXAMPLE I

In the case of baths, each of which contains a wetting agent mixture in a quantity of 1 g./l. of wash-active substance (WAS), the decomposition of foam is measured according to the foam test method 53 902 of the German Industrial Standards (DIN). The foam is produced with 25 beats in 25 seconds, and the height of the foam is measured in cc., the measures being read immediately after churning and after some minutes. The values obtained are compiled in the following Tables I and II. For determination of the wetting values according to the funnel method, a standardized circular cotton fabric is placed on the solution (containing 1 g. of WAS per liter) and then the period of time is measured until the cotton fabric sinks.

As wetting agent mixtures pour in foam formation there were used according to the invention:

Mixture A

	Percent
Addition product of 8 mols of ethylene oxide and 1 mol of iso-tridecyl alcohol	5.4
Urethane of the formula $C_8H_{17}OC(O)N(C_8H_{17})C_2H_4SO_3Na$	3.6
Sodium salt of hexadecylsulfonic acid (prepared by sulfochlorination and saponification of a straight-chain paraffin oil with an average of 16 carbon atoms)	18.6
Stearic acid	1.7
Sodium hydroxide solution (of 33% strength)	0.8
Sodium hexametaphosphate	0.4
Tri-isobutyl-phosphate	0.9
2-ethylcapronic acid ester of an octanol obtained by oxo-synthesis	8.6
Water	60

Wetting value in water free from salt: 8.6 seconds; wetting value in 0.88% sodium hydroxide solution containing per liter 30 g. of sodium chloride: 17 seconds.

6

Mixture B

	Percent
Product obtained by addition of 8 mols of ethylene oxide to 1 mol of isotridecyl alcohol	5.7
Urethane $C_8H_{17}OC(O)N(C_8H_{17})C_2H_4SO_3Na$	2.8
Sodium salt of hexadecylsulfonic acid (as in mixture A)	16.8
Stearic acid	1.7
Sodium hydroxide solution (of 33% strength)	0.8
Sodium hexametaphosphate	0.5
Tri-isobutyl-phosphate	1.0
2-ethylcapronic acid-2-ethylhexyl ester	6.7
Water	64.0
Wetting value in water free from salt: 8.5 seconds; wetting value in 0.88% sodium hydroxide solution containing per liter 30 g. of sodium chloride: 14.8 seconds.	

Mixture C

	Percent
Product obtained by addition of 8 mols of ethylene oxide to 1 mol of isotridecyl alcohol	5.7
Urethane $C_8H_{17}OC(O)N(C_8H_{17})C_2H_4SO_3Na$	2.8
Sodium salt of hexadecylsulfonic acid (as in mixture A)	16.8
Stearic acid	1.7
Sodium hydroxide solution (of 33% strength)	0.8
Sodium hexametaphosphate	0.5
Tri-isobutyl-phosphate	1.0
2-ethylcapronic acid-2-ethylbutyl ester	6.7
Water	64.0
Wetting value in water free from salt: 9 seconds; wetting value in 0.88% sodium hydroxide solution containing per liter 30 g. of sodium chloride: 12.6 seconds.	

TABLE I

Mixture	Distilled water		Height of foam in cc. in—0.88% NaOH		0.88% NaOH plus 30 g. of Na_2SO_4 per liter	
	Immediately	After 2 minutes	Immediately	After 2 minutes	Immediately	After 2 minutes
A ₁ -----	320	60	550	350	520	370
A-----	100	(1)	200	50	400	120
B ₁ -----	300	50	500	130	500	150
B-----	200	(2)	400	70	450	80
C-----	200	(3)	450	70	450	70

¹ After 0 30 sec.

² After 20 0 sec.

³ After 10 0 sec.

For the purpose of comparison, the mixtures A₁ and B₁ were prepared, which correspond to mixtures A and B but do not contain 2-ethylcapronic acid esters.

Mixture D

	Percent
Product obtained by addition of 8 mols of ethylene oxide to 1 mol of iso-tridecyl alcohol	5.3
Urethane $C_8H_{17}OC(O)N(C_8H_{17})C_2H_4SO_3Na$	6.9
Stearic acid	1.7
Sodium hydroxide solution (of 33% strength)	0.7
Tri-isobutyl-phosphate	1.8
Sodium hexametaphosphate	0.4
Sodium salt of an alkylbenzene-sulfonate (the alkyl radical of which has a straight chain with 12 carbon atoms)	12.0
2-ethylhexyl ester of 2-ethylcapronic acid	7.2
Water	64.0

Wetting value in water free from salt: 3-4 seconds; wetting value in 0.88% sodium hydroxide solution: 5-6 seconds.

Mixture E

	Percent
Product obtained by addition of 8 mols of ethylene oxide to 1 mol of isotridecyl alcohol	5.3
Urethane $C_8H_{17}OC(O)N(C_8H_{17})C_2H_4SO_3Na$	6.9
Stearic acid	1.7
Sodium hydroxide solution (of 33% strength)	0.7
Tri-isobutylphosphate	1.8
Sodium hexameta-phosphate	0.4
Sodium salt of an alkylbenzene-sulfonate (the alkyl radical of which has a straight chain with 12 carbon atoms)	12.0
2-ethylhexyl ester of dimethylisopropyl-acetic acid	7.2
Water	64.0
Wetting value in water free from salt: 4-5 seconds; wetting value in 0.88% sodium hydroxide solution: 5-6 seconds.	

Mixture F

	Percent
Product obtained by addition of 8 mols of ethylene oxide to 1 mol of isotridecyl alcohol	5.5
Urethane $C_8H_{17}OC(O)N(C_8H_{17})C_2H_4SO_3Na$	7.2
Stearic acid	1.9
Sodium hydroxide solution (of 33% strength)	0.8
Tri-isobutylphosphate	1.9
Sodium hexametaphosphate	0.4
Sodium salt of hexadecylsulfonic acid (prepared by sulfoxidation of a straight-chain paraffin oil of an average of 16 carbon atoms)	13.4
Isopropanol	4.7
2-ethylcapronic acid ester of octanol obtained by oxo-synthesis	7.5
Water	56.7
Wetting value in water free from salt: 4-5 seconds; wetting value in 0.88% sodium hydroxide solution: 6-7 seconds.	

Mixture G

	Percent
Product obtained by addition of 8 mols of ethylene oxide to 1 mol of isotridecyl alcohol	5.5
Urethane $C_8H_{17}OC(O)N(C_8H_{17})C_2H_4SO_3Na$	7.2
Stearic acid	1.9
Sodium hydroxide solution (of 33% strength)	0.8
Tri-isobutylphosphate	1.9
Sodium hexametaphosphate	0.4
Sodium salt of hexadecylsulfonic acid (as in mixture F)	13.4
Isopropanol	4.7
2-ethylcapronic acid ester of 2,6-dimethylheptanol-4	7.5
Water	56.7
Wetting value in water free from salt: 4-5 seconds; wetting value in 0.88% sodium hydroxide solution: 6-7 seconds.	

TABLE II

Mixture	Height of foam in cc. in—		
	Distilled water after 10 seconds	0.88% NaOH after 1 minute	After 5 minutes
D ₁	20	150	100
D ₂	0	100	30
E	0	100	45
F ₁	20	550	200
F ₂	0	300	75
G	0	300	20

For the purpose of comparison the mixtures D₁ and F₁ were prepared which correspond to mixtures D and F but do not contain 2-ethylcapronic acid esters.

Example 2

A tent cloth which is dyed through only with difficulty is padded with a liquor containing 20 g./l. of the dyestuff C.I. No. 71000 (cf. Color Index, vol. 3, 1956, 2nd edi-

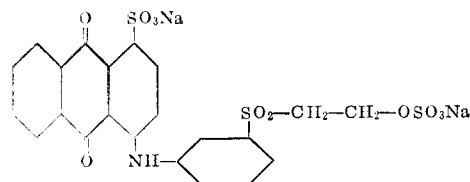
tion) in a finely divided form which is particularly suitable for padding liquors, as well as 10 g./l. of wetting agent mixture C described in Example 1.

Padding is carried out at a temperature of 20° C. The squeezing effect of the double roller padding machine amounts to 80%. After padding, drying and completion of the dyeing by vatting, the dyeing obtained is well penetrated by the dyestuff.

The same method of operation was applied while using, for comparison, liquors containing (a) 4.45 g./l. of a commercially available wetting agent containing as active ingredient about 80% of the sodium salt of dibutyl-naphthalene-sulfonic acid (the amount of wetting agent used thus corresponds in active substance to 10 g. of wetting agent mixture C); (b) no wetting agent. When proceeding according to method (a) the merchandise is only insufficiently penetrated by the dyestuff. The dyeing obtained without addition of wetting agents is unsatisfactory and cannot be used.

Example 3

Several samples of the tent cloth mentioned in Example 2 which is dyed through only with difficulty, are padded at 20° C. on a double roller padding machine with a squeezing effect of 60% with padding liquors containing 30 g./l. of a reactive dyestuff of the following structure



and 3 g./l. of a phthalocyanine reactive dyestuff obtained by reaction of copper phthalocyanine-(3)-tetrasulfonic acid chloride with the acid sulfuric acid ester of β -hydroxyethyl-(4-amino)-phenylsulfone according to the method described in Example 1 of the German patent specification No. 1,179,317 laid open to public inspection; and (a) no wetting agent; (b) 4.45 g./l. of a commercially available wetting agent containing as active ingredient about 80% of the sodium salt of dibutyl-naphthalene-sulfonic acid (the amount used corresponds to 10 g. of the wetting agent mixture C as regards the active substance; (c) 10 g./l. of the wetting agent mixture C described in Example 1.

The merchandise is rolled up and abandoned overnight (for at least 16 hours). It is then rinsed with cold water, acidified with acetic acid, rinsed hot at 80° C., soaped for 10 minutes while boiling with 2 g./l. of an alkylphenyl-polyglycol ether and then rinsed with warm and with cold water.

When dyeing without addition of a wetting agent (a) the dyeing obtained is very weak and uneven. The merchandise is not penetrated by the dyestuff. Compared with dyeing (c) dyeing (b) shows a considerably weaker tint and is less penetrated by the dyestuff.

Moreover, an addition of the wetting agent according to the invention eliminates the difficulties which may be caused by the foam formation of the padding liquor. When using instead of mixture C the wetting agent mixture A described in Example 1 there is obtained a dyeing of equal quality.

Example 4

The levelling action of the wetting agent according to the invention is shown by the following tests:

Ground dyeing.—6 × 10 g. of a bleached cotton yarn are pre-dyed for 45 minutes at 60° C. with 2% of the bluish green indanthren dyestuff bis-benzanthrene-perithiophene in a goods-to-liquor ratio of 1:20 with addition of 16 ml./l. of sodium hydroxide solution (38° Bé.) and 5 g./l. of sodium dithionite, squeezed, oxidized, rinsed, centrifuged and dried.

Levelling-up test.—10 g. each of the cotton yarn dyed in this manner and 10 g. of a bleached cotton yarn are treated for 45 minutes at 60° C. in one bath at a goods-to-liquor ratio of 1:20, with liquors of the following composition:

	1	2	3	4	5	6
32.5% sodium hydroxide solution, cc./l.....	16	16	16	16	16	16
Sodium dithionite, g./l.....	5	5	5	5	5	5
Auxiliary mixture (C) (cf. Example 1), g./l.....	1	2				
Auxiliary agent (I), g./l.....				0.45	0.9	

It is evident that with the use of auxiliary mixture (C) a good levelling-up effect is obtained between the ground dyeing and the undyed yarn added, whereas without the addition of auxiliary agents or when adding auxiliary agent (I) only very little of the dyestuff migrates to the white material.

Auxiliary agent (I) is a commercially available wetting agent containing as active substance about 80% of the sodium salt of dibutyl-naphthalene-sulfonic acid. The content of active substance corresponds to that of mixture C.

Instead of mixture C there may be used with an equally good effect mixture B or mixture E (cf. Example 1).

Example 5

Into a testing device which works according to the principle of the hank dyeing machine there are introduced at 20° C. and 70° C. respectively.

(a): Grey cotton yarn	g--	10
Distilled water	cc--	2000
Wetting agent mixture C (cf. Example 1)	g--	6
(b): Grey cotton yarn	g--	10
Distilled water	cc--	2000
Commercially available wetting agent containing as active substance about 80% of the sodium salt of dibutyl-naphthalene-sulfonic acid (the amount of active substance corresponding to that of 6 g. of the wetting agent mixture mentioned sub (a)	g--	2.7
(c): Grey cotton yarn	g--	10
Distilled water	cc--	2000

The following wetting values were found:

Test (a)—		45
Temperature:		
20° C.	sec--	18
70° C.	sec--	16
Test (b)—		50
Temperature:		
20° C.	sec--	30
70° C.	sec--	45
Test (c)—		55
Temperature:		
20° C.	min--	Over 30
70° C.	min--	7

In test (c) the yarn floats for a long time on the surface of the liquor. Test (a) shows a considerable reduction of the wetting time as compared with test (b). Moreover, the addition of wetting mixture (c) which is poor in foam formation offers the advantage that even at a

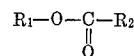
high speed of circulation and at a high temperature no foam formation can be observed on the liquor.

Instead of mixture C there may be used with equal success 5 g. each of mixture G or F.

We claim:

1. A wetting agent showing a levelling action and reduced formation of foam, containing the following components:

(a) aliphatic, carboxylic acid esters of the formula



wherein R₁ is an alkyl radical, having 4-18 carbon atoms, R₂ is an alkyl radical having 4-18 carbon atoms and wherein at least 1 of these alkyl radicals shows at least 1 ramification of 1-4 carbon atoms,

(b) phosphoric acid esters of aliphatic alcohols having 4 to 8 carbon atoms or said phosphoric acid esters which are partially saponified,

(c) fatty acids or soaps, and

(d) wetting agents selected from the group consisting of addition products of 6-30 mols of alkylene oxide, having 2-3 carbon atoms in the alkylene radical and 1 mol of a high molecular aliphatic alcohol or 1 mol of an alkyl phenol containing at least 1 alkyl radical with 4-9 carbon atoms, alkali metal salts of alkyl sulphuric acid esters having 8-18 carbon atoms in the alkyl radical, alkali metal salts of aliphatic and aliphatic-aromatic sulphonic acids, and a mixture of these compounds.

2. A wetting agent as defined in claim 1, containing 0.5 to 4 parts by weight of component (a) 0.05 to 2 parts by weight of component (b) and 0.05 to 1 part by weight of component (c) per 10 parts by weight of component (d).

3. A wetting agent as defined in claim 1, containing 4 to 30% of component (a), 0.1 to 20% of component (b), 0.1 to 10% of component (c) and 60-95% of component (d), referred to the weight of the dry mixture.

4. A process for dyeing, printing, and pad dyeing of textile materials which comprises adding to the dye baths, printing pastes or padding liquors a wetting agent having a levelling action and reduced formation of foam as defined in claim 1.

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