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3,627,475

LEVELLING AGENTS FOR AND PROCESS FOR COLOURING A FIBROUS NATURAL POLY-AMIDE WITH REACTIVE DYES

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Int. Cl. D06p 3/14

U.S. Cl. 8—54

10 Claims

ABSTRACT OF THE DISCLOSURE

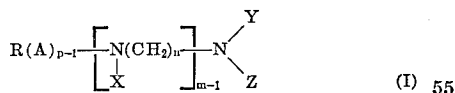
A levelling agent for colouring a fibrous natural polyamide with a reactive dye is constituted by an alkoxyated amine or an addition product thereof with a polybasic acid, or a quaternization product thereof, or an esterification product thereof (especially a sulphation product), or an etherification product thereof, said alkoxyated amine being similar to previously used levelling agents for similar purposes, except that the alkoxyated portion contains both ethylene oxide and propylene oxide groups, butylene oxide groups being optionally present in addition to said ethylene oxide and propylene oxide groups; the colouring may be effected, e.g., by dyeing, padding or printing and the natural polyamide is preferably wool, e.g. in the form of yarn or cloth.

The present invention relates to a process for colouring, e.g. by dyeing, padding or printing, fibrous material of natural polyamides with reactive dyes and to articles resulting from said process.

In the dyeing of wool with reactive dyes it is known to use levelling agents consisting of products obtained by the addition of ethylene oxide or propylene oxide to fatty amines or fatty aminoalkylamines.

It has now been found, in accordance with the invention, that it is possible to obtain products, which are more effective in the dyeing of fibrous material from natural polyamides with reactive dyes than the known products, by using as levelling agent an addition product to the said amines of not only one of the said alkylene oxides but of both of them and/or butylene oxide.

The present invention thus provides a process for colouring, e.g. by dyeing, padding or printing, fibrous material of a natural polyamide with a reactive dye, characterized in that the colouring is effected in the presence of an alkoxyated amine of the formula



or an addition product thereof with a polybasic acid, wherein

R is a hydrocarbon residue of a high molecular weight fatty acid,

A is $-\text{CO}-$, $-\text{OCH}_2\text{CH}_2-$, $-\text{COO}-\text{CH}_2-\text{CH}_2-$, $-\text{O}-\text{CH}_2\text{CHOHCH}_2-$, or $-\text{CO}-\text{NH}-(\text{CH}_2)_n$

X is $\{\text{C}_x\text{H}_{2x-1}\}_m\text{H}$

Y is $\{\text{C}_y\text{H}_{2y-1}\}_n\text{H}$ or $\text{R}-\text{A}-$

Z is $\{\text{C}_z\text{H}_{2z-1}\}_t\text{H}$ or $\text{R}-\text{A}-$

m is an integer of from 1 to 6,

n is an integer of from 2 to 6,

p is 1 or 2,

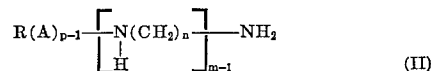
each of r, s and t independently of one another is an integer of from 1 to 200, and

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each of x, y and z independently of one another is 2, 3 or 4,

with the proviso that at least one but not more than 100 ethylene oxide groups and at least one but not more than 200 alkylene oxide groups with 3 or 4 carbon atoms must be present in the compound of the Formula I.

The compound of the Formula I may be produced by reacting the appropriate alkylene oxides with an amine of the formula



wherein

each of R, (A), m, n and p has the above significance, and the resulting compound is acylated with a polybasic acid when an acylated product is required.

Examples of suitable amines of the Formula II, in which $p=1$, are tallamine, aminopropyltallamine, aminoethyltallamine and also amines shown in Table 1 given hereinafter under the designation of AM Index, further dodecyl-, tetradecyl-, cetyl-, stearyl-, oleyl-, arachinyl-, behenyl- and lignocerylamine, or polyamines produced by aminoalkylation of the above mentioned amines, for example alkylaminoethylamines and alkylaminopropylamines.

The addition of the alkylene oxides may be effected according to methods known per se, for example in the presence of catalysts, e.g. alkali metal hydroxides, at ordinary or superatmospheric pressure and temperatures of from 100 to 170° C.

It is possible to add the alkylene oxides in any desired sequence. For example, ethylene oxide may be added first and then propylene oxide together with any butylene oxide which may be used, or propylene oxide may be added first together with any butylene oxide used and only then ethylene oxide or said oxides may be added simultaneously or in alternating manner. When simultaneous addition is effected, it is possible to use mixtures containing ethylene oxide and propylene oxide and, when applicable, butylene oxide.

The resulting addition products may, furthermore, be quaternized with dimethyl sulphate or similar quaternization agents, for example diethyl sulphate, methyl chloride or benzyl chloride, halogen carboxylic acids or their esters or amides, or esterification may be effected with low molecular weight carboxylic acids or preferably, with polybasic inorganic acids, for example with sulphuric acid using a suitable sulphation agent, for example sulphamic acid, or etherification may be effected with a salt of a halogen carboxylic acid.

The products used in the process of the invention, or their salts, quaternization and/or acylation products may be added to the dyebath in an amount of 0.01 to 5% based on the goods to be dyed, addition being preferably effected before dyeing. Dyeing may be carried out in the usual way and with the help of usual additives at the boiling temperature or, alternatively, at temperatures of from 50° C. up, e.g. up to 90° C.

The compounds of the Formula I are liquid to paste-like compounds which are soluble or dispersible in water or dilute acids. By reactive dyes are meant those which contain at least one reactive group, for example the ethyleneimide-, epoxy-, vinyl-, vinyl-sulphonic- or acrylic acid groups, the halogen triazine- or halogenpyrimidine groups.

It will be appreciated that the process of the invention may be effected with the products of the Formula I above in the form of their ethers, esters, salts or quaterni-

zation products and accordingly the use of these ethers, esters, salts and quaternization products is included in the present invention.

In the following examples the temperatures are stated in degrees centigrade and all parts and percentages are by weight.

EXAMPLES 1 to 69

Examples 1-30 (Table 2) show the production of compounds of the Formula I wherein $p=1$ in tabular form; the method of producing the compounds in itself is known, the general conditions being as indicated above. Table 1 shows the amine starting material used for the production of the compound I listed in Table 2. In both Table 1 and 2 R signifies the alkyl residue of tallow fatty acid, R_1 indicates the alkyl residue of coconut oil fatty acid and R_2 signifies the cetyl residue. In Table 2 the first column, headed "Adjuvant" shows the number of the compound of Formula I, the second column shows the starting material amine of the Formula II (i.e. AM index according to Table I), the third, fourth and fifth columns show the number of mols of alkylene oxide which were used per mol of amine of the Formula II in order to produce the "Adjuvant."

In manner similar to Table 2, there are listed in Table 3 (Examples 31-69) compounds of the Formula I in which $p=2$, but in this case there are 8 columns present which give the following information:

Column:

- 1 ---- No. of adjuvant.
- 2 ---- Fatty acid reacted with amine of column 3,
- 3 ---- Amine of column III.
- 4 ---- No. of mols of amine of column III reacted with 1 mol of fatty acid.
- 5 } Indicate respectively the number of mols of
- 6 } the various alkylene oxides added to the
- 7 } reaction product of fatty acid and amine.
- 8 ---- ("Remarks") shows any acylation agent and its amount.

TABLE 1

AM 1...	R-NH-(CH ₂) ₃ -NH-(CH ₂) ₃ -NH ₂
AM 2...	R-NH-(CH ₂) ₃ -NH-(CH ₂) ₃ -NH-(CH ₂) ₃ -NH ₂
AM 3...	R ₁ -NH-(CH ₂) ₂ -NH-(CH ₂) ₂ -NH ₂
AM 4...	R-NH(CH ₂) ₂ -NH-(CH ₂) ₂ -NH-(CH ₂) ₂ -NH ₂
AM 5...	R-NH(CH ₂) ₂ -NH(CH ₂) ₂ -NH(CH ₂) ₂ -NH(CH ₂) ₂ -NH ₂
AM 6...	R-NH(CH ₂) ₂ -NH(CH ₂) ₂ -NH-R

TABLE 2

Adjuvant	1 mol of amine (AM index)	No. of mols of—			Remarks
		1,2-propylene oxide	Ethylene oxide	1,2-butylene oxide	
1.....	AM 1	24	11	-----	
2.....	AM 1	7	14	-----	
3.....	AM 2	15	21	-----	
4.....	AM 2	79	21	-----	
5.....	AM 2	200	100	-----	
6.....	AM 2	20	10	5	Plus 1 mol HOSO ₂ Cl.
7.....	AM 2	169	31	-----	
8.....	AM 3	10	12	-----	
9.....	AM 4	15	20	2	Plus 1 mol NH ₂ SO ₃ H.
10.....	AM 5	200	100	-----	
11.....	AM 5	8	14	-----	
12.....	AM 6	15	20	1	
13.....	AM 1	4	4	-----	
14.....	AM 2	4	8	-----	
15.....	AM 3	2	6	-----	
16.....	AM 5	6	14	-----	
17.....	AM 1	-----	6	2	
18.....	AM 4	1	5	1	
19.....	AM 6	2	6	1	Plus 1 mol NH ₂ SO ₃ H.
20.....	AM 2	-----	15	20	Do.
21.....	AM 7	15	21	-----	
22.....	AM 7	-----	20	20	
23.....	R-NH ₂	1	1	-----	
24.....	R-NH ₂	1	1	1	Do.
25.....	R-NH(CH ₂) ₃ -NH ₂	3	5	-----	
26.....	Same as above	3	15	-----	
27.....	do	-----	10	5	
28.....	R-NH(CH ₂) ₂ -NH ₂	10	5	1	
29.....	R-NH ₂	-----	5	3	
30.....	R-NH(CH ₂) ₃ -NH ₂	3	10	3	Plus 1 mol H ₂ SO ₄ .

TABLE 3

Adju- vant	1 mol of fatty acid amine	Amine	No. of mols of—			Remarks	
			Amine	1,2- propyl- ene oxide	Ethen- oxide		1,2- butyl- ene oxide
31.....	Oleic acid.....	DT	1.1	14	21	-----	
32.....	do.....	DT	1.1	14	21	-----	Plus 1.25 mol NH ₂ SO ₃ H.
33.....	do.....	DT	1.1	100	100	-----	
34.....	do.....	AD	1.1	10	15	2	
35.....	do.....	TT	1.1	15	25	2	Plus 2 mol HOSO ₂ Cl.
36.....	do.....	TP	-----	-----	-----	-----	
37.....	do.....	TP	1.1	200	100	-----	
38.....	do.....	PH	1.1	20	40	20	Plus 1 mol NH ₃ SO ₂ H.
39.....	do.....	-----	-----	-----	-----	-----	
40.....	do.....	ML	1	14	20	-----	
41.....	Stearic acid.....	DT	0.5	10	25	-----	Plus 1.25 ml NH ₂ SO ₃ H.
42.....	do.....	DT	1	20	30	10	Plus 1 mol H ₃ PO ₄ .
43.....	do.....	TN	1	10	25	-----	
44.....	do.....	TN	2	10	25	-----	
45.....	do.....	DA	1	15	25	-----	
46.....	do.....	DA	2	15	25	-----	
47.....	do.....	DPT	1	14	21	-----	
48.....	do.....	DPT	1	-----	21	15	
49.....	Behenic acid.....	DT	1.2	10	30	-----	
50.....	C ₉ -C ₁₁ fatty acid.....	DT	1.1	14	21	2	
51.....	Tallow fatty acid.....	DT	1.2	200	100	-----	
52.....	do.....	PH	0.5	20	21	-----	
53.....	Coconut oil fatty acid.....	DT	1.1	10	11	-----	
54.....	Naphthenic acid.....	DT	1.1	10	11	2	
55.....	Stearic acid.....	HMD	1.1	14	21	-----	
56.....	Oleic acid.....	AD	1.1	3	5	-----	
57.....	do.....	DT	1.1	4	5	1	Plus 1 mol NH ₂ SO ₃ H.
58.....	do.....	ML	1	2	1	-----	

TABLE 3—Continued

Adjunct	1 mol of fatty acid amine	Amine	No. of mols of—				Remarks
			Amine	1,2-propylene oxide	Ethylene oxide	1,2-butylene oxide	
59	Coconut oil fatty acid	PD	1.1	5	5	2	Plus 1 mol HOSO ₂ Cl.
60	Tallow fatty acid	DT	1.1	5	12	6	Plus 1 mol NH ₂ SO ₂ H.
61	do	DT	1.1	5	10	6	
62	C ₇ -C ₁₁ -fatty acid	DT	0.5	5	5	6	Plus 1 mol H ₂ SO ₄ .
63	Stearic acid	PH	0.33	8	11	21	Plus 1 mol NH ₂ SOH ₃ .
64	do	TP	1.1	6	12	6	Do.
65	Behenic acid	DT	1.5	14	12	21	
66	Stearic acid-amide	1 mol	1.1	15	20	21	
67	Stearic acid	DB	1.1	14	21	21	
68	do	DP	1.1	14	21	21	
69	do	OD	1	14	21	21	

In Table 3 the letters in the third column signify the amines as listed below

DT—diethylenetriamine

AD—ethylenediamine

TP—tetraethylenepentamine

TT—triethylenetetramine

PH—pentatethylenhexamine

ML—monohydroxyethylaminoethylamine

TN—triethanolamine

DA—diethanolamine

PD—1,3-propylenediamine

DPT—di-1,3-propylenetriamine

HMD—1,6-hexamethylenediamine

DB—1,4-diaminobutane

DP—1,5-diaminopentane

OD—C₁₈H₃₅—O—CH₂CHOHCH₂—
NH—C₂H₄—NH—C₂H₄—NH₂

Further examples for the production of compounds of the Formula I wherein $p=1$ are the following Examples 70 to 90.

EXAMPLE 70

48 parts of ethylene oxide and thereafter 139 parts of propylene oxide are added to 36 parts of a commercially available amine mixture having the following composition:

palmityl-aminopropylamine—about 30%

stearyl-aminopropylamine—about 30%

oleyl-aminopropylamine—about 40%.

The addition is effected in known manner at a temperature of from 120–160° C. There results a product *a*.

EXAMPLE 71

132 parts of ethylene oxide and 232 parts of propylene oxide are added to 72 parts of the amine mixture described in Example 70. 65 parts of the resulting reaction product are reacted with 3.6 parts of amidosulphonic acid for 6 hours at 100° C. and a product *b* results in this way.

EXAMPLE 72

768 parts of ethylene oxide are added to 300 parts of the amine mixture described in Example 70. 230 parts of propylene oxide are then added to 65 parts of the resulting adduct. There is thus obtained a product *c*.

EXAMPLE 73

232 parts of propylene oxide and then 132 parts of ethylene oxide are added to 72 parts of the amine mixture described in Example 70. 100 parts of the resulting reaction product are reacted with 6.6 parts of butylene oxide at 140–170° C. In this way a product *d* is obtained.

EXAMPLE 74

75.6 parts of ethylene oxide and subsequently 22 parts of propylene oxide are added to 117 parts of the product *c*, so that a product *e* is obtained.

EXAMPLE 75

116 parts of propylene oxide are added to 71 parts of a commercially available addition product of 10 mols of

ethylene oxide to 1 mol of stearylamine; product *f* is obtained thereby.

EXAMPLE 76

20 938 parts of ethylene oxide are added to 20 parts of the amine mixture mentioned in Example 70. 100 parts of the resulting product are then reacted with 70.5 parts of butylene oxide. In this way a product *g* is obtained.

EXAMPLE 77

25 21 mols of ethylene oxide and 119 mols of propylene oxide are added to 1 mol of the amine mixture mentioned in Example 70. The end product is product *h*.

EXAMPLE 78

30 20 mols of propylene oxide and 15 mols of ethylene oxide are added to 1 mol of the amine mixture mentioned in Example 70. In this way a product *i* is obtained.

EXAMPLE 79

35 While stirring well 18 g. of phosphorus pentoxide are added during 1 hour at 50–60° C. to 100 g. of product *i*. Subsequently the mixture is heated for a further 2 hours at 90–100° C. In this way product *i* (1) is obtained.

EXAMPLE 80

45 25 ml. of water are added to 50 g. of the product *i* (1) and neutralization with a 30% sodium hydroxide solution is effected to give a pH value of 7.0. Subsequently 15 ml. of N sodium hydroxide solution are added and the mixture is heated for 1 hour at 95–100° C. Subsequently neutralization is effected and the water is removed in a vacuum. In this way a product *i* (2) is obtained.

EXAMPLE 81

50 2.5 g. of finely pulverized solid sodium hydroxide are added to 50 g. of the product *i*. The resulting mixture is stirred for about 2 hours at 40–50° C. and 2.8 g. of monochloroacetic acid are stirred in slowly thereafter. 55 Stirring is continued for a further hour at 50° C. and subsequently for a further three hours at 75–80° C. In this way a product *i* (3) is obtained.

EXAMPLE 82

60 1 mol of the product *i* is quaternized in the usual way with 1.25 mols of monochloroacetic acid. A product *i* (4) is obtained.

EXAMPLE 83

Product *i* (5) is a reaction product of 1 mol of the product *i* with 1.25 mols of maleic acid anhydride.

EXAMPLE 84

Product *k* is an addition product of 179 mols of propylene oxide and 21 mols of ethylene oxide to 1 mol of the amine mixture mentioned in Example 70.

EXAMPLE 85

5 mols of propylene oxide, then 11 mols of ethylene oxide and finally 5 mols of propylene oxide are added

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to 1 mol (415 g.) of a commercially obtainable amine mixture having the following composition:

stearyl-aminopropylamine—about 25%
 arachinyl-aminopropylamine—about 35%
 behenyl-aminopropylamine—about 40%

In this way a product 1 is obtained.

EXAMPLE 86

25 mols of propylene oxide and 25 mols of ethylene oxide are added to 1 mol of the amine mixture mentioned in Example 70. In this way a product *m* is obtained.

EXAMPLE 87

A product *n* is an addition product of 25 mols of propylene oxide and 11 mols of ethylene oxide to 1 mol of N-dodecyl-aminopropylamine.

EXAMPLE 88

20 mols of propylene oxide, 10 mols of ethylene oxide and 3 mols of butylene oxide are added to 1 mol of dodecylamine. A product *o* is obtained.

EXAMPLE 89

30 mols of propylene oxide and 20 mols of ethylene oxide are added to 1 mol of N-hexadecylethylenediamine ($C_{16}H_{33}NH-CH_2-CH_2-NH_2$). A product *p* results.

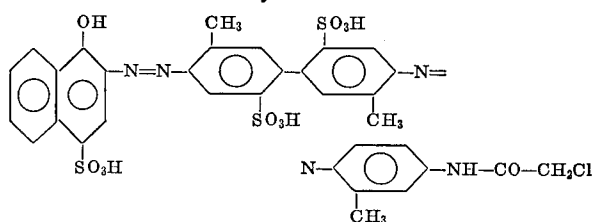
EXAMPLE 90

200 mols in all of propylene oxide and 100 mols in all of ethylene oxide are added to 1 mol of the amine mixture mentioned in Example 70. A product *r* is obtained.

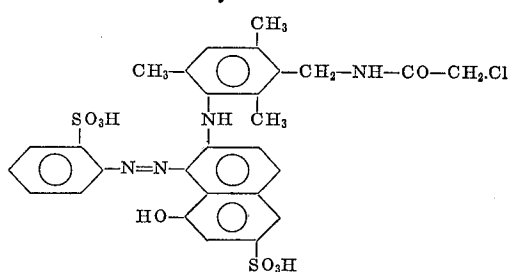
DYEING EXAMPLES

In order to carry out the examples given hereinafter the dyestuffs used correspond to the following formulae, —TCPY signifying the trichloropyrimidine residue derived from tetrachloropyrimidine.

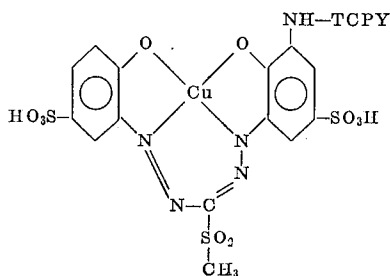
Dyestuff A



Dyestuff B

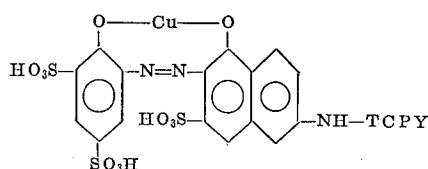


Dyestuff C

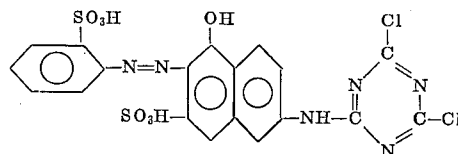


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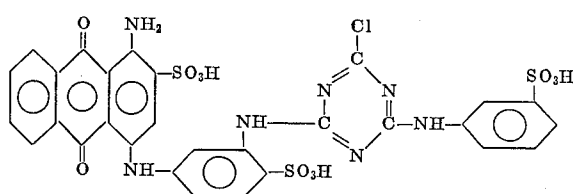
Dyestuff D



Dyestuff E



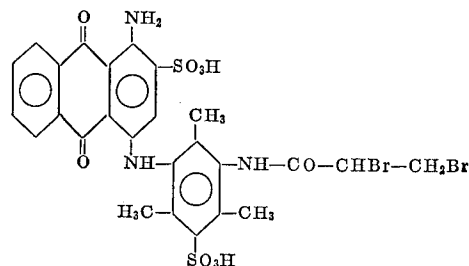
Dyestuff F



Dyestuff G

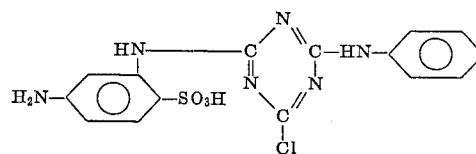
1,2-cobalt complex of the sodium salt of 1-2'-hydroxy-5' - nitrophenylazo - 2 - hydroxy - 3 - trichloropyrimidyl-aminonaphthalene-7,3'-disulphonic acid.

Dyestuff H

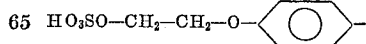


Dyestuff J

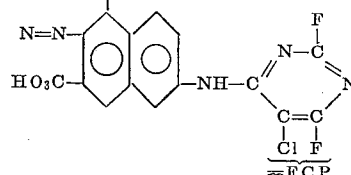
The dyestuff J is obtained by the condensation of 1 mol of copper phthalocyaninetetrasulphonylchloride with 1-2 mol of the following compound



Dyestuff K



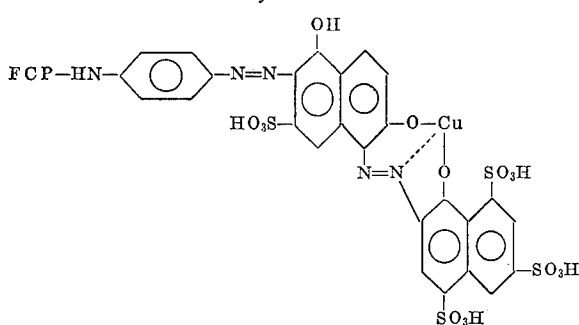
70



75

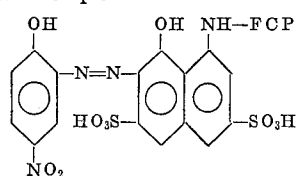
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Dyestuff L



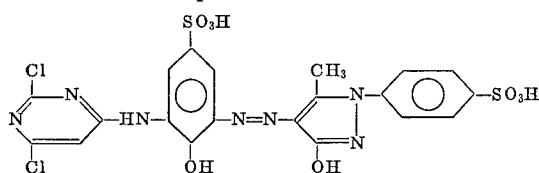
Dyestuff M

1:2-chromium complex of



Dyestuff N

1:2-chromium complex of



EXAMPLE 1

A dyebath is prepared from:

5000 parts of water,
2 parts of the dyestuff A,
5 parts of sodium sulphate,
3 parts of acetic acid and
1 part of the adjuvant 1.

100 parts of loose wool are entered at 50° C. into the bath, heating to the boil during the course of 45 minutes is effected and dyeing is continued for 1 hour at 95–100° C. A level scarlet red dyeing results. The dyebath then no longer contains any dye. When the adjuvant 1 is not present in the dyebath, the dyeing of the wool is not level and, furthermore, the dyestuff has not been absorbed completely on the wool.

When one of the adjuvants 2–30 is added to the dyebath instead of the adjuvant 1, there is obtained likewise a level dyed wool.

EXAMPLE 2

Woollen cloth is dyed at a liquor ratio of 1:40 in a bath containing, based on the cloth, 3% of dyestuff B, 1.5% of acetic acid, 5% of sodium sulphate and 0.75% of the adjuvant 1. Otherwise dyeing is effected as stated in Example 1 and a level red dye results. Similarly, level dyeings are obtained when using, instead of the adjuvant 1, for example 1 part of the adjuvant 26, 32, 44 or 53. When the said adjuvants are not present in the bath, non-level dyeings are obtained.

EXAMPLE 3

100 parts of woollen cloth are placed into 4000 parts of a bath containing 4 parts of acetic acid, 5 parts of sodium sulphate and 1 part of the adjuvant 31. The woollen cloth is pretreated for 20 minutes at a temperature of 50° C. Thereafter 2 parts of the dyestuff C are added to the bath. Heating to the boil is effected during 45 minutes and dyeing is subsequently carried out for 1 hour at the boil. A level dyeing is obtained. A level dyeing is also obtained when a similar amount of each of the

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adjuvants listed in Table 2 and 3 is present in the bath instead of the adjuvant 31. In the absence of the said adjuvants non-level dyeings are obtained.

EXAMPLE 4

Example 3 is repeated with a similar success, but this time, instead of the dyestuff C, dyeing is effected with the same quantity of dyestuff D.

EXAMPLE 5

Example 3 is repeated, but this time, instead of the dyestuff C, the same amount of dyestuff E is used. A level and full orange dyeing is obtained. In the absence of the adjuvant a skittery dyeing is obtained.

EXAMPLE 6

Dyeing according to Example 3 is repeated but instead of the dyestuff C, 3 parts of the dyestuff F are used. A level blue dyeing results. In the absence of an adjuvant a strongly skittery dye material results.

EXAMPLE 7

100 parts of woollen cloth are placed into 4000 parts of a dyebath containing 4 parts of acetic acid, 5 parts of sodium sulphate and 0.5 part of the adjuvant 31. The cloth is placed in the bath at a temperature of 50° C. and pretreated for 10 minutes. At this stage 3 parts of the dyestuff G are added and heating to the boil during 45 minutes is effected and dyeing is carried out for 1 hour at the boil. A level dye of woollen cloth results.

When using, in place of adjuvant 31, the same quantity of each of the adjuvants 32–55 a likewise level dyed woollen cloth results. Furthermore, when dyestuff G is replaced with 3 parts of the dyestuff A, a similarly level dyed woollen cloth is obtained. Without the presence of the adjuvants mentioned the woollen cloth shows a non-level dyeing.

EXAMPLE 8

Example 3 is repeated, but this time, instead of dyestuff C, 2 parts of dyestuff H are added and dyeing is not effected at 95–100° C., but at temperatures between 78 and 83° C. Level dyed wool is obtained.

EXAMPLE 9

The procedure is as described in Example 3, but the dyestuff mentioned therein is replaced with 3 parts of the dyestuff J. A level dyeing results.

However, when dyeing is effected in the absence of the adjuvant, the dyeing is non-level.

EXAMPLE 10

Using the dyestuff F a printing paste is prepared having the following composition:

40 parts of dyestuff F,
60 parts of urea,
30 parts of adjuvant 31,
30 parts of acetic acid (40%),
20 parts of turpentine oil,
190 parts of tragacanth thickener 60:1000 and
630 parts of water.

This printing paste is used for printing by the Vigoureux process on worsted woollen material in the usual way, steaming during 50 minutes is effected twice, the usual rinsing is effected and finishing carried out. The resulting printed wool has very good fastness properties of which there may be mentioned especially acid over dyeing fastness, potting fastness and fastness to drops of water.

EXAMPLE 11

100 parts of woollen yarn are placed in to 4000 parts of a dyeing liquor containing 2 parts of acetic acid, 5

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parts of sodium sulphate and 1 part of adjuvant 32. At a temperature of 50° C. pretreatment of the woollen yarn is effected for 20 minutes. 2 parts of the dyestuff K are then added to the bath. Heating to the boil is effected during 45 minutes and dyeing at the boil is carried out for 1 hour. A level dyeing results. A level dyeing is likewise obtained when using, instead of adjuvant 31, similar quantities of each of the adjuvants 32-55.

A level dyed wool is likewise obtained when using, instead of the dyestuff K, 3 parts of the dyestuff L or 5 parts of the dyestuff M for dyeing. Without the presence of the stated adjuvants, the dyeings are clearly not level.

EXAMPLE 12

The procedure is as in Example 11, but the dyestuff K is replaced with the same amount of the dyestuff N and, instead of woollen yarn the same quantity of woollen cloth is used. Level dyeings result. Without the presence of one of the stated adjuvants the dyeing is not level.

When the adjuvants are not present in the dyebath, the dyestuff is only incompletely adsorbed.

EXAMPLE 13

A dyebath is prepared from

5000 parts of water,
2 parts of dyestuff A,
5 parts of sodium sulphate,
3 parts of acetic acid and
1 part of the product *a*.

100 parts of loose wool are added to the bath at 50° C., heating to the boil is effected during 45 minutes and dyeing is continued during 1 hour at 95-100° C. A level scarlet red dyeing results. At that time dyestuff is no longer present in the dyebath. When the product *a* is not present in the dyebath, the wool does not become level dyed and the dyestuff, furthermore, is not completely adsorbed onto the wool.

When, instead of the product *a*, the same amount of each of the products *b*, *c*, *d*, *e*. or *f* is added to the dyebath, wool is obtained which is likewise level dyed.

EXAMPLE 14

Woollen cloth is dyed at a liquor ratio of 1:40 in a bath which contains, based on the weight of the cloth, 3% of dyestuff B, 1.5% of acetic acid, 5% sodium sulphate and 0.75% of the product *a*. Otherwise the dyeing is effected as stated in Example 1 and a level red dyeing is obtained. Level dyeings are likewise obtained when there is used, instead of the products *a*, 1 part of each of the products *b*, *c*, *d* or *f*. When the said products are not present in the bath, dyeings result which are not level.

EXAMPLE 15

100 parts of woollen cloth are put into 4000 parts of a bath containing 4 parts of acetic acid, 5 parts of sodium sulphate and 1 part of the product *a*. Pretreatment of the woollen cloth is effected at 50° C. for 20 minutes. 2 parts of dyestuff C are then added to the bath. During 45 minutes heating to the boil is effected and subsequently dyeing is carried out at the boil for 1 hour. A level dyeing results. A level dyeing is likewise obtained when, instead of the product *a*, there is used 1.5 parts of each of the products *b*, *c*, *d*, *e* or *f* in the bath. In the absence of the said products dyeings are obtained which are not level.

EXAMPLE 16

The procedure of Example 15 is repeated with a similar success, except that the dyestuff C is replaced with the same amount of the dyestuff D to effect dyeing.

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EXAMPLE 17

The procedure of Example 15 is repeated, but the same amount of dyestuff E is used instead of the dyestuff C. A level and full orange dyeing results. In the absence of the said adjuvant a skittery dyeing results.

EXAMPLE 18

Dyeing in accordance with Example 15 is repeated but, instead of dyestuff C, 3 parts of dyestuff F are used. A level blue dyeing results. In the absence of one of the products *a*, *b*, *c*, *d*, *e* and/or *f* a very skittery dyeing on the material results.

EXAMPLE 19

100 parts of woollen cloth are placed into 4000 parts of a dyebath containing 4 parts of acetic acid, 5 parts of sodium sulphate and 0.5 part of the product *a*. The cloth is put into the bath at a temperature of 50° C. and pretreated for 10 minutes. At this time 3 parts of the dyestuff A is added, heating to the boil during 45 minutes is effected and dyeing is effected for 1 hour at the boil. A level dyed woollen cloth results. A level dyed wool also results when adding, instead of the product *a*, one part of each of the products *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i*, *il*, *i2*, *i3*, *i4*, *i5*, *k*, *l*, *m*, *n*, *o*, *p*, *q*, or *r*. Furthermore, when the dyestuff G is replaced with 3 parts of the dyestuff A, a woollen cloth is obtained which is likewise level dyed. Without the presence of the said products the woollen cloth is not level dyed.

EXAMPLE 20

Example 15 is repeated. However, instead of the dyestuff C, 2 parts of the dyestuff H are added and dyeing is not effected at 95-100° C., but at temperatures between 78 and 83° C. Wool is obtained which is level dyed.

EXAMPLE 21

The procedure of Example 15 is repeated, but the dyestuff therementioned is replaced with 3 parts of the dyestuff J. A level dyeing is obtained.

On the other hand, when dyeing is effected in the absence of the adjuvant, the dyeing is not level.

EXAMPLE 22

The procedure of Example 10 is repeated but, instead of adjuvant 31, the same amount of product *a* is used; the Vigoureux print obtained in this way had good properties as described in Example 10.

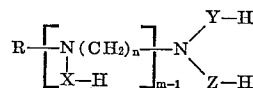
EXAMPLE 23

Using 1 part of product *a*, instead of adjuvant 32, the procedure of Example 11 is repeated; the results obtained are similar to those of Example 11.

EXAMPLE 24

The procedure is as in Example 13, but the dyestuff K is replaced with the same quantity of the dyestuff N and, in place of the woollen yarn, the same amount of woollen cloth is used. Level dyeings are obtained. Without the presence of the said adjuvant the dyeing is not level. When the products are not present in the dyebath, the dyestuff is only incompletely adsorbed on to the woollen cloth.

It will be appreciated that among the alkoxyated amines of the Formula I above are products corresponding to the formula



in which

R is the hydrocarbon residue of a fatty acid with from 12 to 24, e.g. 16-22, carbon atoms,

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n is an integer from 2 to 3,

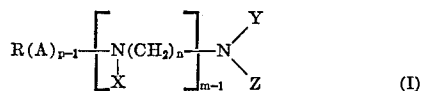
m is an integer from 1 to 2,

and each of X, Y and Z represents a polyalkylenoxide residue consisting of some alkylene portions with 2 carbon atoms, the remainder having 3 to 4 carbon atoms, with the proviso that the sum of the alkylene portions with 3 to 4 carbon atoms must be 7 to 200 and that of the ethylene portions must be 2 to 100 and the further proviso that the sum of all the alkylene groups in X, Y and Z must be greater than 20,

and the use of these materials in the process of the invention is advantageous.

I claim:

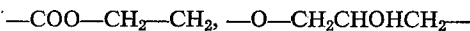
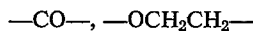
1. A process for colouring fibrous material of natural polyamides with reactive dyes wherein the colouring is effected in the presence of a substance selected from alkoxylated amines of the formula



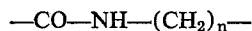
their reaction products with polybasic acids, salts thereof, quaternization products thereof and etherification products thereof, wherein

R is the hydrocarbon residue of a high molecular weight fatty acid of the formula $R-\text{COOH}$,

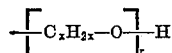
A is a group selected from the class consisting of



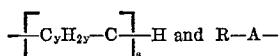
or



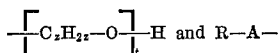
X is



Y is selected from the class consisting of



Z is selected from the class consisting of



m is an integer of from 1 to 6,

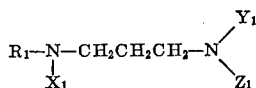
n is an integer from 2 to 6,

p is selected from 1 and 2,

each of r , s and t independently of one another is an integer of from 1 to 200, and

each of x , y and z independently of one another is selected from 2, 3 and 4, with the proviso that at least one but not more than 100 ethylene oxide groups and at least one but not more than 200 alkylene oxide groups with 3 to 4 carbon atoms must be present in the compound of the Formula I.

2. A process according to claim 1, in which the colouring is effected in the presence of a product corresponding to the formula



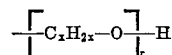
in which

R_1 is the hydrocarbon residue of a fatty acid of the for-

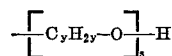
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mula $R_1-\text{COOH}$ wherein R_1 contains from 16 to 22 carbon atoms,

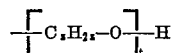
X_1 is



Y_1 is

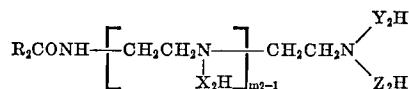


Z_1 is



and x , y , z , r , s and t are chosen in such a way that said product contains 11 to 25 ethenoxy and 10 to 25 1,2-propenoxy groups in its molecule.

3. A process according to claim 1, in which the colouring is effected in the presence of a product corresponding to the formula



in which

$R_2\text{CO}$ is the radical of a fatty acid with R_2 containing 16 to 22 carbon atoms

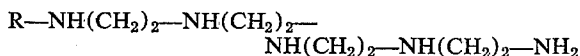
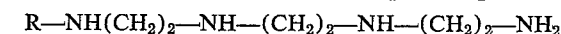
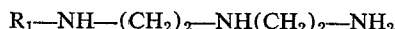
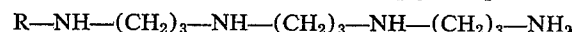
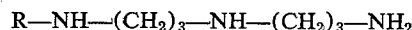
each of the symbols X_2 , Y_2 and Z_2 represents an alkyleneoxy residue, all of which together are constituted by from 1 to 100 ethenoxy and from 2 to 100 1,2-propenoxy groups

and m_2 is selected from 1 and 2.

4. A process according to claim 1, in which the compound of Formula I is present in a partially sulphated form.

5. A process according to claim 1, in which said fibrous material to be coloured with a reactive dye is wool.

6. A process according to claim 1, in which the amine portion of said alkoxylated amine is selected from tallamine, aminopropyltallamine, aminoethyltallamine, amines of the formulae

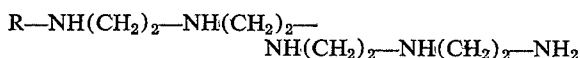
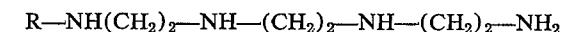
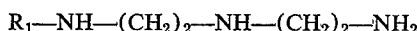
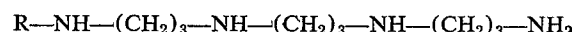
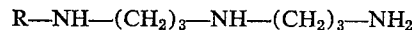


and



and dodecyl-, tetradecyl-, cetyl-, stearyl-, oleyl-, arachinyl-, behenyl- and lignocerylamine.

7. A process according to claim 1, in which the amine portion of said alkoxylated amine is selected from polyamines produced by aminoalkylation of tallamine, aminopropyltallamine, aminoethyltallamine, amines of the formulae



and



and dodecyl-, tetradecyl-, cetyl-, stearyl-, oleyl-, arachinyl-, behenyl- and lignocerylamine.

8. A process according to claim 1, in which the colouring is effected in the presence of a quaternization product of said alkoxylated amine produced by means of a

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quaternization agent selected from diethyl sulphate, methyl chloride, benzyl chloride, a halogen carboxylic acid, a halogen carboxylic acid ester and a halogen carboxylic acid amide.

9. A process according to claim 1, in which said alkoxylated amine contains a plurality of ethylene oxide, propylene oxide and butylene oxide residues.

10. A process according to claim 1, in which said fibrous material of a natural polyamide is coloured by dyeing in a dyebath containing at least one reactive dye in the presence of said alkoxylated material.

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U.S. Cl. X.R.

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