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PROCESS FOR THE FAST DYEING OF NATURAL AND ARTIFICIAL POLYAMIDE FIBERS WITH WATER-SOLUBLE METAL-CONTAINING AZO DYESTUFFS

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The present application is a continuation-in-part of copending application Ser. No. 625,594, filed December 3, 1956 (abandoned since the filing of the present application).

With the development of the synthetic nitrogenous fibers there has been a marked increase in the consumption of wool dyestuffs. There is a particularly heavy demand for water-soluble dyestuffs capable of dyeing nitrogenous fibers such as wool, silk, man-made nitrogenous fibers of casein, and synthetic polyamide and polyurethane fibers in shades fast to light, washing and milling. Experience has shown that for these purposes water-soluble, metal-containing azo dyestuffs are the most suitable. It is very difficult, however, to apply the members of these dyestuff classes to the fiber so as to ensure uniform affinity and level-dyeing. Furthermore, it is recognized that the optimum pH value for wool dyeing is about 4 to 5.5. Wool dyed in this pH region is well protected physically, and its elastic properties remain unimpaired. The spinning properties, too, are favorably affected and the goods manufactured from such dyed wools have a soft, lofty hand. When wool is dyed at a pH of about 4 to 5.5 without a dyeing assistant, however, the resulting dyeings are not only unlevel but also of poor fastness to crocking. In view of this it has been a long-standing aim of research to establish a dyeing process whereby water-soluble, metal-containing azo dyestuffs, can be dyed from a weakly acid dyebath in level shades of good fastness to crocking.

It has now been found that natural and artificial polyamide fibers can be dyed in the weakly acid region with water-soluble metal-containing azo dyestuffs, applied singly or in combination with each other, to give level and fast shades and that the dyeings on natural or artificial polyamide fibers obtained with such dyestuffs can be stripped from the said fibers.

The natural and artificial polyamide fibers are dyed from or the dyeings stripped in an aqueous dye-liquor containing:

(*a*) A mixture of a basic water-soluble polyglycol ether, produced by combining ethylene oxide with a polyamine of the formula

$$R_1—O—CH_2—CHOH—CH_2—R_2 \quad (I)$$

wherein

R_1 stands for an alkyl radical which contains at least 8 carbon atoms, an alkenyl radical with 8 to 18 carbon atoms, an alkylphenyl or dialkylphenyl radical which contains at least 5 carbon atoms in the alkyl group or a higher alkylpolyglycol ether radical, and

R_2 for the radical of an aliphatic di-or triamine, which is attached through a nitrogen-atom to the $—CH_2—$ group, and if desired by quaternating the thus obtained addition product, and of a water-soluble polyglycol ether carboxylic acid of the formula

$$R_3—O—(CH_2—CH_2—O)_x—CH_2—COOH \quad (II)$$

wherein

R_3 stands for an alkyl or alkenyl radical which contains at least 16 carbon atoms or an alkylaryl or dialkylaryl radical which contains more than 13 carbon atoms, and

x, for an integer greater than 19,

(*b*) An organic acid.

(*c*) An alkali metal salt of an organic acid, which can act as a buffer substance, and

(*d*) At least 10%, calculated on the weight of the fiber, of an alkali metal sulfate. Dyeing is carried out by adding the dyestuff solution to the dyeing liquor at a temperature below the boil or at boiling temperature, dyeing being conducted at boiling temperature. Stripping is carried out by adding the dyeing to the stripping medium containing the ingredients listed above at a temperature below the boil or at boiling temperature, stripping being conducted at boiling temperature.

Under the term basic water-soluble polyglycol ethers as here defined are to be understood products such as those enumerated by way of example in the following Table I. They are characterized by the fundamental substance used for their formation, the number of mols of ethylene oxide reacted with the said fundamental substance, and the number of quaternated, preferably with dimethyl sulfate, nitrogen atoms. In Table II the water-soluble polyglycol ethercarboxylic acids are characterized by the fundamental substance (R_3) employed in their formation and by the number of mols of ethylene oxide (x) reacted with the said fundamental substance.

TABLE I

No. of the polyglycol ether	Fundamental Substance	Number of Added Mols of Ethylene Oxide	Number of Quaternated Nitrogen Atoms
1	$C_8H_{17}—OCH_2—CHOH—CH—N_3HC_2H_4NHC_2H_4NH_2$	8.5	----------
2	$C_{12}H_{25}OCH_2—CHOHCH_2NHC_2H_4NH—C_2H_4NH_2$	8.5	----------
3	$C_{12}H_{25}OCH_2—CHOHCH_2NHC_2H_4NH—C_2H_4NH_2$	8.5	3
4	$C_{16}H_{33}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	6.7	----------
5	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	5.5	----------
6	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	8.5	----------
7	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	10	----------
8	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	12	----------
9	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	14.8	----------
10	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	20	----------
11	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	24	----------
12	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	30	----------
13	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	40	----------
14	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	5	3
15	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	8.5	3
16	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	12	1
17	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	12	2
18	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	12	3
19	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	14.5	1

TABLE I—Continued

No. of the polyglycol ether	Fundamental Substance	Number of Added Mols of Ethylene Oxide	Number of Quaternated Nitrogen Atoms
20	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	14.5	2
21	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	14.5	3
22	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	17	1
23	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	17	2
24	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	17	3
25	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	20	2
26	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	20	3
27	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	25	3
28	$C_{18}H_{35}OCH_2CHOHCH_2NH(CH_2)_6NH_2$	5	----
29	$C_{18}H_{35}OCH_2CHOHCH_2NH(CH_2)_6NH_2$	8.5	----
30	$C_{18}H_{35}OCH_2CHOHCH_2NH(CH_2)_6NH_2$	12	----
31	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NH_2$	4.5	----
32	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NH_2$	4.5	2
33	$C_{18}H_{35}OCH_2CHOHCH_2NHCH_2CH(CH_3)NH_2$	4	----
34	$C_{18}H_{35}OCH_2CHOHCH_2NHCH_2CH(CH_3)NH_2$	4	2
35	$C_{16}H_{33}OCH_2CHOHCH_2NHC_3H_6NH(CH_2)_3NH_2$	5	----
36	$C_{18}H_{35}OCH_2CHOHCH_2NHCH_2CH_2CH_2NHCH(CH_3)_2$	8	----
37	$C_{18}H_{35}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NHC_2H_4NH_2$	10	----
38	$C_{18}H_{35}(OC_2H_4)_{10}OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	10	----
39	$(C_5H_{11})_2C_6H_3OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	6.8	----
40	$(C_5H_{11})_2C_6H_3OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	6.8	3
41	$C_{12}H_{25}(C_6H_4)OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	5	----
42	$C_{12}H_{25}(C_6H_4)OCH_2CHOHCH_2NHC_2H_4NHC_2H_4NH_2$	12.5	----

TABLE II

No. of the polyglycol ethercarboxylic acid	Fundamental Substance R_3—OH	Number of Added Mols of Ethylene Oxide x
43	$C_{18}H_{35}OH$	20
44	$C_{18}H_{35}OH$	24
45	$C_{18}H_{25}OH$	30
46	$C_{18}H_{25}OH$	40
47	$(C_8H_{17})_2C_6H_3OH$	40
48	$(C_9H_{19})_2C_6H_3OH$	30
49	$C_9H_{19}C_6H_4OH$	60
50	$C_{12}H_{25}C_6H_4OH$	40

Of the organic acids which may be employed in the present process, propionic, citric and, above all acetic acid rank first in interest. Alkali-metal salts of organic acids which act as buffers are for example sodium and potassium acetate, propionate and citrate, sodium acetate being the preferred. Potassium sulfate or, preferably, sodium sulfate serve as alkali-metal sulfates, whereby an amount of 20 to 40%, calculated on the weight of the fiber, is preferred.

The dyeing process is carried out by adding the dyestuff solution to the dyeing medium, into which the natural or artificial polyamide fibers have been previously entered, advantageously at about 50–60° C. The dye-bath is then heated to the boil slowly, e.g. in the course of about 30–60 minutes, and the material dyed to shade at boiling temperature, for which a further period of about 30 to 60 minutes is necessary.

The resulting dyeings are level and fast to crocking. In addition they possess the other excellent properties commonly provided by water-soluble metal-containing azo dyestuffs, for instance very good fastness to washing, milling and perspiration. As regards the light fastness of the dyeings the alkalyarylpolyglycol ether carboxylic acids Nos. 47, 48, 49 and 50 behave in a very favorable manner.

In comparison with existing dyeing methods the new process presents a further advantage in that it precludes "smearing," the expression used to describe the streaky dyestuff precipitates on the wall of the dye vessel, a phenomenon often observed in acid dyebaths. Another merit of the present process is the fact that the dyeings do not bleed when rinsed in water, as is often the case with the known methods.

The surprisingly good results of the new process are due to a combination of three factors, by which more is accomplished than could have been predicted from the sum of their properties; namely the combination of the mixture of the basic polyglycol ether and of the polyglycol ether-carboxylic acid conforming to the present definition with the buffered acidity of the dyebath and the distinctive action which the relatively high content of alkali-metal sulfate exerts on the course of the dyeing process. If one of these three factors is omitted, the buffer substance or the previously mentioned polyglycol ether mixture or the alkali-metal sulfate, unlevel dyeings are generally obtained.

The following examples illustrate the invention. All parts and percentages specified therein are by weight; the temperatures are in degrees centigrade.

Example 1

100 parts of a wool hank are entered into a dyebath at 50° containing 5,000 parts of water, 1.5 parts of Lanasyn Red BL, 0.1 part of the basic polyglycol ether No. 8 and 0.9 part of the polyglycol ether carboxylic acid No. 44, 5 parts of sodium acetate, 2 parts of 100% acetic acid and 25 parts of sodium sulfate. The dyebath is brought to the boil in the course of 50 minutes and is then boiled for a further 30 minutes. After this time 90% of the total dyestuff employed is exhausted. The resulting dyeing is level and is a very bright red in shade.

Similarly, very level red dyeings are obtained when the Lanasyn Red BL used in this example is replaced by Lanasyn Red 2GL. For the production of level yellow

to orange shades the following dyestuffs are eminently suitable: Lanasyn Yellow 3GL, Lanasyn Yellow GLN, Lanasyn Yellow 2RL and Lanasyn Orange RLN.

The basic polyglycol ether No. 8 may be replaced by an equal quantity of one of the basic polyglycol ethers of Table I and the polyglycol ether carboxylic acid No. 44 by an equal amount of one of the polyglycol ether carboxylic acids Nos. 43 or 45 to 50. The resultant dyeings are level and of bright shade.

Example 2

100 parts of loose wool are dyed in a machine with circulating liquor. The dye liquor is composed of 5,000 parts of water, 1 part of Lanasyn Dark Violet RL, 0.1 part of the basic polyglycol ether No. 9 and 0.8 part of the polyglycol ether carboxylic acid No. 45, 5 parts of sodium propionate, 4 parts of 100% propionic acid and 25 parts of sodium sulfate. The liquor is brought to the boil over 50 minutes then boiled for a further 30 minutes. After this time 95% of the dyestuff initially present is exhausted. The dyeing thus obtained is level and of a bright violet shade.

The basic polyglycol ether No. 9 may be replaced by one of the basic polyglycol ethers Nos. 10 to 25 and the polyglycol ether carboxylic acid No. 45 by one of the polyglycol ether carboxylic acids Nos. 43, 44, and 46–50; the resulting dyeings show a level violet shade.

In place of Lanasyn Dark Violet RL, Lanasyn Bordeaux RL, Lanasyn Brown RL, Lanasyn Brown 3RL and Lanasyn Gray BL may be employed with equal success.

Example 3

100 parts of wool slubbing are dyed in a dyeing machine with circulating liquor. The dye liquor is made up of 5,000 parts of water, 2 parts of Lanasyn Yellow GLN, 0.1 part of the basic polyglycol ether No. 8 and 1 part of the polyglycol ether carboxylic acid No. 48, 5 parts of sodium acetate, 3 parts of 100% acetic acid and 25 parts of sodium sulfate. The liquor is heated to the boil in the course of 50 minutes and boiling continued for another 30 minutes. After this time 90–95% of the dyestuff employed is exhausted. A level dyeing of bright yellowish shade is obtained.

Instead of the basic polyglycol ether No. 8 one of the basic polyglycol ethers Nos. 5, 6, 7, 9, 10, 11, 12 and 13 may be used with the same degree of success, while the polyglycol ether carboxylic acid No. 50 may be replaced by one of the polyglycol ether carboxylic acids Nos. 43–47, 49 and 50.

Example 4

100 parts of loose tippy dyeing wool are dyed in a machine with circulating liquor. The dye liquor consists of 5,000 parts of water, 0.3 part of Lanasyn Red BL, 0.6 part of Lanasyn Brown 3RL, 0.3 part of the basic polyglycol ether No. 8 and 1.2 parts of the polyglycol ether carboxylic acid No. 49, 5 parts of sodium acetate, 2.5 parts of 80% acetic acid and 25 parts of sodium sulfate. The dyeing procedure is the same as that described in Examples 1 to 3. The red-brown dyeing which is obtained shows good uniformity of shade between the fiber roots and tips.

Level red-brown dyeings are also obtained when the basic polyglycol ether No. 8 is replaced by one of the basic polyglycol ethers Nos. 5, 6, 7, 9 to 13 or 19 to 27 and the polyglycol ether carboxylic acid No. 49 by one of the polyglycol ether carboxylic acids Nos. 43 to 48 or 50.

Example 5

100 parts of loose wool are dyed in a machine with circulating liquor from a dyebath containing 0.8 part of Lanasyn Red 2GL. The dyeing is produced in the manner described in Examples 1 to 4 and shaded with 0.2 part of Lanasyn Yellow GLN, this being added to the dyebath at 80°. The red-orange dyeing thus obtained is level and of bright shade.

Example 6

100 parts of a wool fabric are immersed in a liquor in a winch prepared with 5,000 parts of water, 2 parts of Lanasyn Red BL, 1.5 parts of the basic polyglycol ether No. 7, 1 part of the polyglycol ether carboxylic acid No. 43, 5 parts of sodium citrate, 30 parts of a 10% aqueous solution of citric acid and 25 parts of sodium sulfate. The dye liquor is heated to the boil in the course of 50 minutes and the material dyed to shade in the way described in Examples 1 to 4. A level and bright red dyeing is obtained.

When the same dyestuff is dyed by the method hitherto used, i.e. from a neutral bath with the addition of 2 parts of ammonium sulfate, the dyeing turns out unlevel and appreciably duller in shade.

Example 7

100 parts of wool fabric are entered into a blind dye liquor composed of 5,000 parts of water, 0.1 part of the basic polyglycol ether No. 8 and 0.9 part of the polyglycol ether carboxylic acid No. 45, 5 parts of sodium acetate, 25 parts of sodium sulfate and 2 parts of 100% acetic acid. The wool is boiled in this bath for 15 minutes, after which time a concentrated solution of 0.5 part of Lanasyn Gray BL and 0.1 part of Lanasyn Yellow GLN is allowed to flow into the boiling bath in the course of 30 minutes. After a further 30 minutes at the boil the material is dyed to a briught, level shade. The basic polyglycol ether No. 8 may be readily replaced by one of the basic polyglycol ethers Nos. 5, 6, 7, 9, 10, 11, 12, 13 and 19 to 27 and the polyglycol ether carboxylic acid No. 45 by one of the polyglycol ether carboxylic acids Nos. 43, 44 and 46 to 50.

When the material is dyed in the same way from a neutral bath with the addition of 2 parts of ammonium sulfate but without the polyglycol ether and the buffer mixture, the dyeing turns out very unlevel.

Example 8

100 parts of a wool fabric dyed with 2.4 parts of Lanasyn Dark Violet RL are boiled for 30 minutes in a blind dyebath containing 5000 parts of water, 0.4 part of the basic polyglycol ether No. 10 and 3.6 parts of the polyglycol ether carboxylic acid No. 50, 5 parts of sodium acetate, 25 parts of sodium sulfate and 2 parts of 100% acetic acid. The treatment causes the dyeing to lose heavily in depth.

The acetic acid may be omitted altogether or reduced in quantity. The basic polyglycol ether No. 10 may be replaced by another of the basic polyglycol ethers of the Table I and the polyglycol ether carboxylic acid No. 49 by another of the polyglycol ether carboxylic acids of the Table II.

Example 9

100 parts of wool fabric are dyed with 1 part of Lanasyn Orange RLN under conditions which result in an unlevel dyeing. The dyed wool fabric is subsequently boiled for 30 minutes in a blind dyebath containing 5000 parts of water, 0.15 part of the basic polyglycol ether No. 8 and 0.85 part of the polyglycol ether carboxylic acid No. 47, 6 parts of sodium acetate, 25 parts of sodium sulfate and 2 parts of 100% acetic acid. The treatment leaves the dyeing with a markedly leveler appearance.

In place of the basic polyglycol ether No. 8 one of the basic polyglycol ethers Nos. 6, 7, 9 to 13, and 19 to 40 will be found equally satisfactory; the polyglycol ether carboxylic acid No. 47 may be replaced by one of the polyglycol ether carboxylic acids Nos. 43 to 46 and 48

to 58. When 1 part of Lanasyn Orange RLN is added to the blind dyebath according to this invention, white wool can be dyed therewith in level orange shades.

Example 10

100 parts of wool are entered into a dye liquor at 50° prepared with 5000 parts of water, 2.4 parts of Lanasyn Bordeaux RL, 25 parts of sodium sulfate, 5 parts of sodium acetate, 2 parts of 100% acetic acid, 0.1 part of the basic polyglycol ether No. 9, 0.45 part of the polyglycol ether carboxylic acid No. 43 and 0.45 part of the polyglycol ether carboxylic acid No. 46. The dyebath is heated to boiling temperature over a period of 45 minutes and dyeing continued for 60 minutes at 100°. A fast, level dyeing of bright Bordeaux shade is obtained.

The basic polyglycol ether No. 9 can be replaced by one of the polyglycol ethers Nos. 5, 6, 7, 8, 10, 11, 12, 13 and 19 to 27 and the mixture of the polyglycol ether carboxylic acids Nos. 43 and 46 by a mixture of the polyglycol ether carboxylic acids of the Table II. In the foregoing examples the number of components in the mixture of polyglycol ethers and polyglycol ether carboxylic acids can be varied as desired.

Example 11

100 parts of a hank of nylon 66 are entered into a dyebath made up of 5000 parts of water, 2 parts of Lanasyn Brown RL, 0.1 part of the basic polyglycol ether No. 8 and 0.9 part of the polyglycol ether carboxylic acid No. 47, 3 parts of sodium acetate, 1 part of 100% acetic acid and 25 parts of sodium sulfate. The dye liquor is raised to the boil in the course of 50 minutes, and the dyebath boiled for a further 40 minutes. After this time 93% of the total dyestuff employed is exhausted. A fast and level brown dyeing is obtained.

When the basic polyglycol ether No. 8 is replaced by one of the basic polyglycol ethers Nos. 6, 7, 9, 10, 11, 12, 13, 19 to 27, and the polyglycol ether carboxylic acid No. 47 by one of the polyglycol ether carboxylic acids of the Table II, a similarly fast and level brown dyeing is obtained. If the dyeing is carried out in a neutral dyebath without a buffer mixture and without a mixture of polyglycol ethers, but with an addition of 4% ammonium sulfate, the bath exhaustion already amounts to 98% after 15 minutes at the boil. However, this rapid exhaustion causes a bad levelling of the dyeings.

The following dyestuffs: Lanasyn Yellow 3GL, GLN, 2RL, Lanasyn Orange RLN, Lanasyn Scarlet GL, Lanasyn Red 2GL, BL, Lanasyn Bordeaux RL, Lanasyn Dark Violet RL, Lanasyn Brown GRL, 3RL and Lanasyn Gray BL, 2BL behave the same as, or similarly to, Lanasyn Brown RL.

Example 12

100 parts of a Perlon fabric are entered into a dyebath containing 5000 parts of water, 2 parts Lanasyn Yellow 3GL, 0.2 part of the basic polyglycol ether No. 6 and 1 part of the polyglycol ether carboxylic acid No. 49, 3 parts of sodium acetate, 1.5 parts of 100% acetic acid and 15 parts of sodium sulfate. The dye liquor is brought to the boil in the course of 50 minutes and is then boiled for 40 minutes. After this time 97% of the dyestuff employed is exhausted. The resultant dyeing is level and bright yellow in shade.

The basic polyglycol ether No. 6 can be replaced by another basic polyglycol ether of Table I and the polyglycol ether carboxylic acid No. 49 by one of the polyglycol ether carboxylic acids Nos. 43 to 48 and 50. Polyurethane fibers are dyed in the same way.

Example 13

100 parts of a silk hank are immersed in a dye liquor at 60° composed of 5000 parts of water, 2 parts of Lanasyn Brown 3RL, 5 parts of sodium acetate, 1 part of 80% acetic acid, 0.15 part of the basic polyglycol ether No. 8 and 0.85 part of the polyglycol ether carboxylic acid No. 50. The temperature of the dye bath is raised over 40 minutes to 90°, during which time a solution of 10 parts of sodium sulfate in 100 parts of water is added in small portions. Dyeing is continued for 15 minutes at 90°, then 2 parts of 80% acetic acid are run into the bath and dyeing completed at the same temperature in 30 minutes. The dyeing thus obtained is level and bright brown.

Should 4 parts of Lanasyn Brown 3RL be used, the amount of sodium sulfate must be increased, e.g. to 15 parts, and the total amount of 80% acetic acid to e.g. 4 parts.

The basic polyglycol ether No. 8 may be replaced without disadvantage by one of the basic polyglycol ethers Nos. 6, 7, 9 to 13, 19 to 27, whilst the polyglycol ether carboxylic acids Nos. 43 to 49 are equally as effective as the polyglycol ether carboxylic acid No. 50.

The dyestuffs in Example 11 can be dyed on silk, individually or in combination, by the procedure described in this example. They yield level and fast shades.

Having thus disclosed the invention, what is claimed is:

1. A process for the fast-dyeing of fibers selected from the group consisting of wool, silk, nylon and Perlon in the weakly acid region with water-soluble, 1:2-metal-containing azo dyestuffs to give level and fast shades, which comprises dyeing the said fibers in an aqueous liquor consisting essentially of (*a*) a mixture of (1) a basic water-soluble polyglycol ether, produced by combining ethylene oxide with a polyamine of the formula

$$C_{18}H_{35}—O—CH_2—CHOH—CH_2—R_2$$

wherein R_2 stands for a member selected from the group consisting of the radical of an aliphatic diamine which contains not more than 6 carbon atoms and is connected to the adjacent —CH_2— group through a nitrogen atom, and the radical of derivatives thereof quaternated with dimethyl sulfate, and (2) a water-soluble polyglycol ether carboxylic acid of the formula

$$R_3—O—(CH_2CH_2O)_x—CH_2—COOH$$

wherein R_3 stands for a member selected from the group consisting of $C_{18}H_{35}$, alkylphenyl with 8 to 12 carbon atoms in the alkyl group thereof, and dialkylphenyl with 8 to 12 carbon atoms in the alkyl group thereof, and x stands for an integer greater than 19; (*b*) an organic acid; (*c*) an acid-binding buffer consisting of an alkali metal salt of an organic acid; (*d*) at least 10%, calculated on the weight of the fiber, of an alkali metal sulfate and (*e*) water, the dyestuff solution being added to the dyeing liquor, containing all the other ingredients, at a temperature below the boil, and conducting the dyeing at boiling temperature up to 100° C.

2. The process for the dyeing of polyamide fibers according to claim 1, wherein the dye liquor contains acetic acid, the sodium salt of acetic acid, 25 percent of sodium sulfate and a mixture consisting of 0.1 percent of the water-soluble polyglycol ether which is the condensation product of

$$C_{19}H_{35}OCH_2CHOH—CH_2—NH—C_2H_4—NH—C_2H_4—NH_2$$

with 12 moles of ethylene oxide, and 0.9 percent of the water-soluble polyglycol ether carboxylic acid of the formula

$$C_{18}H_{35}—O—(CH_2—CH_2—O)_{30}—CH_2—COOH$$

the percent figures being calculated on the weight of the fiber.

3. The process for the fast dyeing of polyamide fibers according to claim 1, wherein the dye liquor contains acetic acid, the sodium salt of acetic acid, 25 percent of sodium sulfate and a mixture consisting of 0.15 percent of the water-soluble polyglycol ether which is the condensation product of

$$C_{18}H_{35}OCH_2CHOH—CH_2—NH—C_2H_4—NH—C_2H_4—NH_2$$

with 12 moles of ethylene oxide, and 0.85 percent of the water-soluble polyglycol ether carboxylic acid of the formula

$$(C_{18}H_{17})_2C_6H_3—O—(CH_2—CH_2—O)_{40}—CH_2—COOH$$

the percent figures being calculated on the weight of the fiber.

4. The process for the fast dyeing of polyamide fibers according to claim 1, wherein the dye liquor contains acetic acid, the sodium salt of acetic acid, 25 percent of sodium sulfate and a mixture consisting of 0.3 percent of the water-soluble polyglycol ether which is the condensation product of

$$C_{18}H_{35}OCH_2CHOH—CH_2—NH—C_2H_4—NH—C_2H_4—NH_2$$

with 12 moles of ethylene oxide, and 1.2 percent of the water-soluble polyglycol ether carboxylic acid of the formula

$$C_9H_{19}C_6H_4—O—(CH_2—CH_2—O)_{60}—CH_2—COOH$$

the percent figures being calculated on the weight of the fiber.

5. The process for the fast dyeing of polyamide fibers according to claim 1, wherein the dye liquor contains acetic acid, the sodium salt of acetic acid, 25 percent of sodium sulfate and a mixture consisting of 0.1 percent of the water-soluble polyglycol ether which is the condensation product of

$$C_{18}H_{35}OCH_2CHOH—CH_2—NH—C_2H_4—NH—C_2H_4—NH_2$$

with 12 moles of ethylene oxide, and 0.9 percent of the water-soluble polyglycol ether carboxylic acid of the formula

$$(C_{18}H_{17})_2C_6H_3—O—(CH_2—CH_2—O)_{40}—CH_2—COOH$$

the percent figures being calculated on the weight of the fiber.

6. The process for the fast dyeing of polyamide fibers according to claim 1, wherein the dye liquor contains acetic acid, the sodium salt of acetic acid, 25 percent of sodium sulfate and a mixture consisting of 0.1 percent of the water-soluble polyglycol ether which is the condensation product of

$$C_{18}H_{35}OCH_2CHOH—CH_2—NH—C_2H_4—NH—C_2H_4—NH_2$$

with 12 moles of ethylene oxide, and 1 percent of the water-soluble polyglycol ether carboxylic acid of the formula

$$(C_9H_{19})_2C_6H_3—O—(CH_2—CH_2—O)_{30}—CH_2—COOH$$

the percent figures being calculated on the weight of the fiber.

7. A process for the fast-dyeing of fibers selected from the group consisting of wool, silk, nylon and Perlon in the weakly acid region with water-soluble, 1:2-metal-containing azo dyestuffs to give level and fast shades, which comprises first introducing the said fibers in an aqueous liquor consisting essentially of (*a*) a mixture of (1) a basic water-soluble polyglycol ether, produced by combining ethylene oxide with a polyamine of the formula

$$C_{18}H_{35}—O—CH_2—CHOH—CH_2—R_2$$

wherein R_2 stands for a member selected from the group consisting of the radical of an aliphatic diamine which contains not more than 6 carbon atoms and is connected to the adjacent —CH_2— group through a nitrogen atom, and the radical of derivatives thereof quaternated with dimethyl sulfate, and (2) a water-soluble polyglycol ether carboxylic acid of the formula

$$R_3—O—(CH_2CH_2O)_x—CH_2—COOH$$

wherein R_3 stands for a member selected from the group consisting of $C_{18}H_{35}$, alkylphenyl with 8 to 12 carbon atoms in the alkyl group thereof, and dialkylphenyl with 8 to 12 carbon atoms in the alkyl group thereof, and x stands for an integer greater than 19; (*b*) an organic acid; (*c*) an acid-binding buffer consisting of an alkali metal salt of an organic acid; (*d*) at least 10%, calculated on the weight of the fiber, of an alkali metal sulfate, and (*e*) water, then adding the dyestuff solution to the dyeing liquor, containing all the other ingredients, at a temperature below the boil, and finally carrying out the dyeing at a boiling temperature up to 100° C.

8. A process for the fast-dyeing of fibers selected from the group consisting of wool, silk, nylon and Perlon in the weakly acid region with water-soluble, 1:2-metal-containing azo dyestuffs to give level and fast shades, which comprises first introducing the said fibers in an aqueous liquor consisting essentially of (*a*) a mixture of (1) a basic water-soluble polyglycol ether, produced by combining ethylene oxide with a polyamine of the formula

$$C_{18}H_{35}—O—CH_2—CHOH—CH_2—R_2$$

wherein R_2 stands for a member selected from the group consisting of the radical of an aliphatic diamine which contains not more than 6 carbon atoms and is connected to the adjacent —CH_2— group through a nitrogen atom, and the radical of derivatives thereof quaternated with dimethyl sulfate, and (2) a water-soluble polyglycol ether carboxylic acid of the formula

$$R_3—O—(CH_2CH_2O)—CH_2—COOH$$

wherein R_3 stands for a member selected from the group consisting of $C_{18}H_{35}$, alkylphenyl with 8 to 12 carbon atoms in the alkyl group thereof, and dialkylphenyl with 8 to 12 carbon atoms in the alkyl group thereof, and x stands for an integer greater than 19; (*b*) an organic acid; (*c*) an acid-binding buffer consisting of an alkali metal salt of an organic acid; (*d*) at least 10%, calculated on the weight of the fiber, of an alkali metal sulfate, and (*e*) water, then adding the dyestuff solution to the dyeing liquor, containing all the other ingredients, at a temperature of about 50° to 60° C., and finally carrying out the dyeing at a boiling temperature up to 100° C.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

'atent No. 3,043,648 July 10, 1962

Hans Martin Hemmi et al.

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

Columns 1 and 2, TABLE I, under the heading "Fundamental Substance", and opposite "1" thereof, for "C_8H_{17}-OCH_2-CHOH-CH-$N_2HC_2H_4NHC_2H_4NH_2$" read -- C_8H_{17}-OCH_2-CHOH-$CH_2NHC_2H_4NHC_2H_4NH_2$ --; column 6, line 33, for "briught" read -- bright --; column 10, line 38, for "R_3-O-(CH_2CH_2O)-CH_2-COOH" read -- R_3-O-(CH_2CH_2O)$_x$-CH_2-COOH --.

Signed and sealed this 4th of June 1963.

(SEAL)
Attest:
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