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PROCESS FOR THE DYEING OF SYNTHETIC POLYAMIDE FIBERS

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ABSTRACT OF THE DISCLOSURE

Process for the dyeing of synthetic polyamide fiber textile material, comprising dyeing the said material with an aqueous dyestuff preparation which contains:

(a) Neutral- to weakly acid-drawing anionic wool dyestuff as coloring agent,

(b) Hydrophilic surface-active dye assistant consisting essentially of, per molecule, a hydrophobic organic radical and at least one polyglycol ether radical;

(c) At least one water-soluble aldehyde condensation product containing basic nitrogen, and

(d) The pH of said preparation at the beginning of dyeing being less than 7.5 but not less than 3.

This invention relates to the dyeing of synthetic polyamide fibers and textiles made up therefrom, in particular to the dyeing of textile fabrics and other articles manufactured from these fibers. The invention also concerns aqueous dyestuff preparations suitable for this dyeing process and, as industrial product, the materials dyed according to the process.

It is known that synthetic polyamide fibers and textiles manufactured therefrom can be dyed with anionic acid wool dyestuffs in fast shades. The term "synthetic polyamides" as used in this specification and the appended claims means polyamides which are produced by polycondensation from polyfunctional organic amines and polycarboxylic acids, e.g. from hexamethylenediamine or decamethylenediamine and adipic acid or sebacic acid, or by addition polymerization from lactams of aliphatic aminocarboxylic acids, e.g. from ε-aminocaprolactam. It is also known that these polyamide fibers and the fabrics produced therefrom dye very differently if, in these fibers, the degree of orientation of the polyamides is different. As the degree of orientation can be influenced by stretching the fibers, often very undesirable streakiness of the dyeings occurs due to uneven mechanical strain of the warp and weft of fabrics. There are also other causes of streakiness such as nonuniform heat-treatment of the fibers or differences in the terminal groupings of the nylon molecules. It is difficult to improve the streaky appearance of such dyeings, for it is well known that the usual levelling agents hitherto used in wool dyeing, e.g. polyglycol ethers of alkanols having 10–20 carbon atoms, alkyl phenols, alkylamines and polyalkylene polyamines substituted by higher alkyl or acyl radicals and having at least 15 ethyleneoxy groups in the polyglycol ether chain or chains, form addition complexes with anionic dyestuffs which have reduced drawing power onto polyamide fibers. Moreover, while these levelling agents serve very well also for the dyeing of synthetic polyamide, particularly in an alkaline dye bath, provided dyeing is performed with uniform dyestuffs of high affinity to the treated fiber, they are unsatisfactory when fashion shades are be dyed with mixtures of dyestuffs under the conditions described, because very light differences in the affinity of the individual dyestuffs to polyamide fibers and in the stability of the dyestuff-polyglycol ether complex lead, particularly on polyamide fabrics to uneven, cloudy, streaky dyeings and, in the case of larger batches, to dyeings with end-to-end and side-to-center unlevelness.

As a consequence of the above mentioned complex formation, dyeing yield is often unsatisfactory because, in certain circumstances, a considerable part of the dyestuff remains in the dyebath. Reproduction of dyeings in identical shades, which is important in industrial practice, suffers thereby, and an undesirable amount of waste is produced.

It has now been found that these disadvantages can be overcome and synthetic polyamide fibers, particularly also textile fabrics and other articles manufactured from these fibers, can be very evenly dyed in all conventionally desired depths with good exhaustion of the dyebaths by using as the latter, or in their preparation, aqueous dyestuff compositions which contain as substantial components:

(a) Neutral to weakly acid drawing anionic wool dyestuff as coloring agent;

(b) A hydrophilic non-ionogenic surface-active polyaminoether which contains a hydrophobic organic radical and at least one hydrophilic polyglycol ether radical, from 0 to not more than about 5 ethyleneoxy groups, of which are C-alkyl and/or C-phenyl substituted; preferred polyamino-ether being defined further below, especially condensation products of formaldehyde with ammonia or Mannich bases;

(c) A water-soluble aldehyde condensation product containing from 1 to 4 basic nitrogen atoms per molecule, preferably hexamethylene tetramine, and

(d) Sufficient acid to adjust the pH value of the dyebath at the beginning of the dyeing treatment to less than 7.5 but not less than 3.

In dyeing of the above-defined fiber materials by the exhaustion process, the dyestuff preparation to be used according to the invention consists of a dye liquor having conventional contents of from about 0.1 to 6% by weight of commercial dyestuff and of 0.5 to 3% by weight of auxiliaries, calculated on the weight of the polyamide material to be dyed. Dyeing is performed at temperatures of about 95° C. to about 130° C. at the boil or under static pressure, and preferably at temperatures of over 100° C. in a closed vessel.

Dyestuff preparations to be used according to the invention contain, apart from dyestuff of the types described further below, a critical dye assistant combination consisting of:

(I) As hydrophilic, surface-active compounds, those which contain, as hydrophobic radical, hydrocarbon radicals such as alkyl or alkenyl radicals having at least 10 and preferably 12 to 18 carbon atoms, alkylaryl radicals the alkyl substituents of which contain at least 5 and preferably 6 to 12 carbon atoms, or alicyclic hydrocarbon radicals, and they contain at least one hydrophilic polyglycol ether group of the above-defined length. The two characteristic moieties of these compounds can be linked together by way of various bridging atoms or groups, for example:

(a) By means of oxygen such as in the polyglycol ethers of higher alkanols and alkenols as well as in higher phenols alkylated in the ring,

(b) By means of sulfur, e.g. in the polyglycol ethers of higher alkylmercaptans and alkenylmercaptans and in the thiophenols the ring of which is higher alkyl-substituted,

(c) By way of nitrogen, e.g. in the polyglycol ethers of higher alkylated or alkenylated primary or secondary aliphatic monoamines or polyamines, or

(d) By the carboxy group —CO—O—, e.g. in the poly-

glycol ethers of higher saturated or unsaturated fatty acids, alkoxy and alkylthio fatty acids having higher alkyl groups, by means of the carbamide group —CO—N<, e.g. in the polyglycol ethers of the amides of carboxylic acids listed above with ammonia monoalkyl-, monohydroxyalkyl- and dihydroxyalkylamines, as well as with aliphatic or alicyclic polyamines, in which a long polyglycol ether chain or several shorter ones can be bound by way of nitrogen.

The polyglycol ethers of higher acylaminoalkyl mono- and polyamines have proved to be particularly valuable in the process according to the invention, particularly those of lauryl-, myristyl-, oleyl-, palmityl-, stearylaminoethylamine, -ethylenediamine, -diethylenetriamine, as well as of higher monoalkyl- or alkenyl- ethylenediamine, -diethylenetriamine, -triethylenetetramine having in all at least 15, preferably more than 25 to about 100 ethyleneoxy radicals, which can be arranged in one sole or in different chains, and their ethyleneoxy groups, some of which can also be alkyl-substituted, particularly methyl-substituted, or phenyl-substituted to strengthen the lipophilic character of this moiety. In the surface active compounds usable according to the invention, the hydrophilic character can be strengthened, if desired, optionally by esterification of aliphatic hydroxyl groups with polybasic inorganic or organic acids to form acid esters or soluble salts thereof. Good results are obtained with technical mixtures of homologous and analogous compounds and mixtures with the soluble salts of acid esters, e.g. of the sulfates, phosphates, maleates, etc. with unesterified compound.

Especially satisfactory results of broad applicability to a great variety of dyestuffs are obtained with those dye assistants in which the component (b), supra, is a nonionogenic capillary active ether, which is obtained by reacting 1 mol of a polyamine of the general formula:

$$L—NH—A(X—A)_m—NH_2$$

wherein:

L represents a lipophilic alkyl or alkenyl radical having 16–18 carbon atoms,

A represents an alkylene radical selected from the group consisting of $—CH_2—CH_2—$ and

$$—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—$$

radicals,

X represents a member selected from the group consisting of —NH— and —O—, and

m represents one of the numbers 0 to 2,

preferably first with 1 mol of styrene oxide, preferably at a temperature of about 100 to 200° C., and then reacting the resulting intermediate in any order desired with 50 to 150 mols, preferably 70 to 100 mols of ethylene oxide and 0 to 2 mols of another oxide selected from the group consisting of styrene oxide and propylene oxide, at a temperature of about 80 to 200° C.; or directly reacting the polyamine of the above general formula with the aforesaid amounts of ethylene oxide and the other oxide; and

(II) As water-soluble aldehyde condensation products containing basic nitrogen those derived from lower aliphatic aldehydes and ammonia or from lower organic amines, especially lower alkyl amines. The preferred condensation product is hexamethylenetetramine.

The mixture of the dye assistants consists of surface-active polyglycol ethers and basic nitrogen-containing aldehyde condensation product, in a weight ratio of about 4:1 to 1:4.

Optimal dyeings on nylon textile materials, free from streakiness and in good yield are obtained when using in the dyeing process according to the invention, a dye assistant mixture consisting of:

(1) A polyaminoether obtained by reacting 1 mol of a polyamine of the general formula:

$$Octadecyl\text{-}NH—CH_2—CH_2—(NH—CH_2—CH_2)_m—NH_2$$

wherein *m* represents one of the numbers 0 to 2,

first with 1 to 2 mols of styrene oxide and then with 70 to 100 mols of ethylene oxide, under the conditions specified hereinbefore, and

(2) Hexamethylene tetramine, in a weight ratio of (1):(2) ranging from about 3:1 to 1:3.

Mixtures consisting of mono-stearyl diethylenetriamine polyglycol ethers having over 30 ethyleneoxy radicals and hexamethylenetetramine in a ratio of about 3:2 to 2:3 are particularly suitable.

The inorganic and, preferably, organic acids usual in dyeing used as acids to adjust the pH of the aqueous dyestuff preparation to the critical range stated hereinbefore, are, for example, sulfuric acid, phosphoric acid or their acid salts such as sodium or potassium bisulfate, mono- and di-sodium or ammonium phosphate, toluene sulfonic acid, tetraline sulfonic acid and, particularly, lower aliphatic carboxylic acids such as formic acid and, preferably, acetic acid. A particularly favorable result is obtained in the process according to the invention when the ratio of the preferred hexamethylenetetramine to an acid which forms a salt therewith, is about one mol of amine per equivalent of acid; acetic acid, formic acid and sulfuric acid are particularly useful as such acids.

A preferred method of the invention is the dyeing, by the exhaustion process, of fabrics or articles made from synthetic fibers which are produced from addition polyamides. This is performed preferably at temperatures of at least 100° C., e.g. under static pressure is a closed vessel and, particularly, at temperatures of over 100° C. to 135° C. Good dyeing yield of very level dyeings in any desired depth are obtained by this method in relatively very short dyeing times. Dyeing is advantageously performed in short dyebaths using a ratio of liquor to textile material of 10:1 to 20:1, the liquor containing about 0.5 to 3% of auxiliaries calculated on the weight of the goods being dyed and depending on the amount of dyestuff or the desired depth of shade.

Large batches of fast and evenly dyed fabrics and articles made from synthetic polyamide are attained by the process according to the invention. The polyamide dyeings attained according to the invention are distinguished by excellent levelness, very good exhaustion of the bath and the dyeings can be reproduced very easily. Also the polyamide part of blended fabrics consisting of synthetic polyamide and other non-polyamide textile fibers can be dyed by the process according to the invention.

It is noteworthy that neither the use of the dye assistants enumerated above under (I) alone, nor the use of hexamethylenetetramine or another compound falling under the definition of (II) given above, permits the production of dyeings on the aforesaid fibers free from streakiness, while, surprisingly, dyeing with the composite dye assistant consisting, according to the invention, of (I) and (II) especially in the above stated weight ratios, leads unexpectedly to perfectly level dyeings, free from streakiness, when using dyestuffs of the classes defined below.

The physico-chemical mechanism of this phenomenon is at present unknown.

As dyestuffs, there are usable in the process according to the invention, practically all neutral to weakly acid drawing anionic wool dyestuffs of the various known classes of fast wool dyestuffs. Particularly suitable in the new dyeing process is the use of neutral to weakly acid drawing azo and azomethine dyestuffs containing heavy metal, whereby fast, level dyeings on fabrics and articles made of synthetic addition polyamide fibers produced from lactams of aliphatic aminocarboxylic acids such as

ε-caprolactam are obtained. Among these dyestuffs are the known azo and azomethine dyestuff complexes of heavy metals of the atomic numbers 24, 27 and 29 which per trivalent heavy metal atom bound in complex linkage, contain more than one complex former—of which at least one is tridentate and colored—or a more than tridentate colored complex former.

Particularly suitable are the chromium and cobalt complexes of o,o'-dihydroxy -monoazo, -disazo or -azomethine dyestuffs, of o-hydroxyl-o'-carboxy mono- or dis-azo dyestuffs, of o-hydroxy-o'-amino mono- or also dis-azo dyestuffs which, per heavy metal atom, contain two identical or different dyestuffs bound in complex linkage. In addition to complex-forming substituents, the dyestuff components of these heavy metal complexes also contain known substituents to promote water-solubility, for example, lower alkylsulfonyl groups such as methylsulfonyl, chloromethylsulfonyl, oxymethylenesulfonyl, ethylsulfonyl, isopropylsulfonyl, n-butylsulfonyl groups, sulfamyl groups such as sulfonic acid amide, sulfonic acid mono- or di-lower alkylamide, lower hydroxyalkylamide, sulfonic acid phenylamide groups, or acylamido groups such as alkylsulfamide or arylsulfamide groups, e.g. methylsulfamide, chloromethylsulfamide, chloroethylsulfamide, toluene sulfamide, acetamide, chloroacetamide, propionylamide, β-chloro- or bromo-propionlyamide, lower alkoxycarbamide groups. Uunder certain conditions, these heavy metal-containing dyestuffs can also contain a salt-forming group which dissociates acid such as the carboxyl, the disulfimide and, particularly, the sulfonic acid groups, but advantageously they only contain one of these groups alone in a so-called 2:1 complex consisting of a monosulfonated and an unsulfonated basic dyestuff bound in complex linkage to a chromimum or cobalt atom. The presence of a sulfonic acid substituent in so-called mixed heavy metal complex dyestuffs is particularly indicated if one of the basic dyestuffs forming the complex is a disazo dyestuff or an azomethine dyestuff containing arylazo groups, or if the dyestuff component containing no sulfonic acid groups also has no substituents which promote water-solubility. Metallized mono- and dis-azo dyestuffs forming tridentate and polydentate metal complexes are also suitable which, per heavy metal atom, contain only one sole colored complex former and, optionally, in addition a non-colored complex former. These are, for example, complex chromium compounds of o-hydroxy-o'-aminoazo dyestuffs of the benzeneazonaphthalene series having a secondary amino group forming the complex, the substituent of which also has complex-forming properties. The copper complexes of metallizable disazo dyestuffs of the formazane series are also very suitable; low-sulfonated copper phthalocyanins having substituents promoting water-solubility of the type listed above can also be used. Of the class of heavy metal-containing dyestuffs, also those types are very suitable which contain, bound to a heavy metal atom, particularly chromium, an unsulfonated, tridentate complex-forming, metallizable azo dyestuff and a colorless complex former which can contain substituents promoting water-solubility; the usual colorless complex formers in these dyestuffs are salicylic acid and, particularly, the amides, alkylamides or phenylamides of sulfosalicylic and sulfocresotic acids. In addition to the complex-forming and the water solubility-promoting substituents, all these heavy metal-containing azo and azomethine dyestuffs can also contain other substituents usual in azo dyestuffs, for example, low alkyl and alkoxy groups, halogens such as fluorine, chlorine or bromine, nitro groups etc. Dyestuffs not containing heavy metal which can be used according to the invention are, among others, neutral to quickly drawing acid wool dyestuffs of the azo series, for example, disazo dyestuffs containing sulfonic acid groups with diphenylether, diphenylamine, phenylnaphthylamine or phenylsulfonyloxyaryl groupings, also neutral or quickly drawing acid wool dyestuffs of the triphenylmethane or diphenyl-indolylmethane series, of the pyrene series, e.g. rhodamines such as halogenated rhodamine dyestuffs, of the anthraquinone series, e.g. the 4,4'-bis - (4 - amino - 3 - sulfo - anthraquinonyl - 1 - amino)-diphenylalkane dyestuffs. These dyestuffs can also contain in their aromatic nuclei substituents conventional in dyestuffs listed above.

Synthetic polyamide fibers which can be evenly dyed according to the invention are, for example, the materials known in the textile industry by the following names:

Nylon 66, a textile fiber from hexamethylene-diamine and adipic acid produced by condensation;

Nylon 610, a textile fiber from the same diamine and sebacic acid, produced by condensation;

Nylon 66/6, a textile fiber from mixed polymers produced by condensation of hexamethylene-diamine and adipic acid and addition of ε-caprolactam;

Nylon 6, a textile fiber produced from addition polymers of ε-caprolactam;

Nylon 11, a textile fiber from ω-aminododecanoic acid produced by condensation, as well as polyamide fibers of the same or similar structure most of which are commercially available.

The preferred polyaminoethers mentioned and others used in the composite dye assistants according to the invention are obtained, for example, from diprimary or diprimary-secondary or diprimary-tertiary alkylene polyamines and from diprimary or diprimary-secondary or diprimary-tertiary di- or triethers by condensing in the heat with an at most equimolecular amount of alkyl, alkylbenzyl, cycloalkyl or alkylcycloalkyl chlorides or bromides or of alkali metal salts of acid sulfates of the corresponding hydroxyl compounds. After liberating the bases obtained with strong alkalis, any more easily volatile components still present are distilled off, advantageously in vacuo, and the mixture of bases which is not easily volatile is used direct for the condensation with styrene oxide.

These starting materials which advantageously contain one primary amino group and, in all, at least 2 but advantageously not more than 4 basic nitrogen atoms, are reacted, according to the invention, first with an equimolecular amount of styrene oxide. In this reaction an amino group, particularly easily a primary amino group, is substituted by the β-hydroxyphenethyl radical, probably by the β-hydroxy-β-phenylethyl radical. The reaction product is then reacted with a low molecular alkylene oxide, in particular with ethylene oxide or propylene oxide or with mixtures of the two, in such amounts and under such conditions that at least 50, in particular in all 70 to 100 alkyleneoxy radicals are introduced. Depending on the desired properties of the end products, it is often advantageous if certain proportions of ethylene oxide and propylene oxide are reacted simultaneously or one after the other with the styrene oxide-polyamine condensation products. The condensation products which contain at least 50 and advantageously more than 70 ethyleneoxy radicals and have a low content of propyleneoxy radicals are generally still sufficiently water-soluble for direct use for the purposes intended. It is often advantageous for an intended use of the condensation products according to the invention if they contain more than one phenylethyleneoxy radical. It is possible, without difficulty, at any stage, i.e. before, during or after the reaction with alkylene oxide, to add single equivalents of styrene oxide. However, in order to attain sufficient water-solubility, it is indicated to limit the number of phenylethyleneoxy groups incorporated. This number should not be greater than the number of hydrogen atoms bound direct to basic nitrogen atoms in the starting material. Advantageously, in all there should not be more than three such groups.

The epoxides are added under the usual conditions. Whereas for the addition of styrene oxide in the first step it is generally sufficient to react the component by

heating to about 100° C. to 200° C. depending on the composition, generally a basic catalyst such as sodium or potassium hydroxide, carbonate or alcoholate, is necessary for the addition of the alkylene oxides. Depending on their reactivity, the alkylene oxides can be incorporated in the solutions of the starting materials and catalysts in inert organic solvents, or in the melts of the starting materials, if necessary under pressure. In general, raised temperatures of, for example 80° C. up to about 200° C. are indicated.

The following examples illustrate the invention. Temperatures are given therein in degrees centigrade. Parts and percentages are by weight unless expressly stated otherwise. C.I. means Colour Index, second edition, 1956, published by the Society of Dyers and Colourists, Bradford, England, and the American Association of Textile Chemists and Colorists, Lowell, Mass., U.S.A.

EXAMPLE 1

A high temperature beam dyeing machine consisting of a closed system fitted with a circulation pump for circulating the liquor both from inside to the outside and vice versa is used. In the vat for the dye liquor in this machine, 1 kg. of a polyglycol ether produced by reacting 90 mols of ethylene oxide with N-stearyl diethylenetriamine and 0.6 kg. of hexamethylenetetramine are dissolved in 1500 liters of water, and the pH of the solution is adjusted to about 4.5 by the gradual addition of about 1.5 kg. of 40%-acetic acid. 110 kg. of warp-knit tricot of nylon 6 wound round the perforated beam are introduced, the apparatus is closed and the circulation pump is set in action. After 10 minutes, a mixture of 1.0 kg. of the chromium-containing dyestuff obtained from 2 mols of 1 - phenyl - 3 - methyl-4-(2'-carboxy-5'-methylsulfonylphenylazo)-5-pyrazolone per chromium gram atom bound in complex linkage, 0.6 kg. of the chromium-containing dyestuff obtained from 2 mols of 1-acetylamino - 7 - hydroxy - 8 - (2' - hydroxy-5'-ethylsulfonylphenylazo) - naphthalene per chromium gram atom, bound in complex linkage, and 0.25 kg. of the chromium-containing dyestuff obtained from 2 mols of 1-phenyl-3-methyl - 4 - (2' - hydroxy-5'-ethylsulfonyl-phenylazo)-5-pyrazolone per chromium gram atom, bound in complex linkage, and 15 liters of hot water is drawn in through the pump system and the liquor is circulated from inside to outside during the whole dyeing process, first for 10 minutes at room temperature (20°), then for 45 minutes while gradually and evenly raising the temperature to 120° and then for 20 minutes at this temperature. The liquor is then allowed to cool to below 100°, the excess pressure is removed and the dyed goods are rinsed with circulating warm and cold water. Goods very evenly dyed in a stone grey-olive shade are obtained. The dyeings are wet- and light-fast.

Very similar results are obtained by using, in this example, instead of the dyestuffs disclosed, commercial products of similar structure, e.g. C.I. Acid Yellow 129, C.I. Acid Black 60 and C.I. Acid Orange 86.

When in this or one of the following examples, 0.1 to 6% calculated on the weight of the textile material to be dyed, of one or more of the commercial dyestuffs given below are used, depending on the desired shade, then similar level and wet-fast dyeings of a corresponding shade are obtained. The following dyestuffs are thus used:

(a) Unsulfonated 1:2 metal complexes of monoazo dyestuffs containing lower alkylsulfonyl groups as groups promoting water-solubility: C.I. Acid Red 259; C.I. Acid Violet 78; C.I. Acid Brown 227; C.I. Acid Red 258; C.I. Acid Black 64;

(b) Monoazo dyestuffs, free from sulfonic acid groups, but having sulfamyl or sulfamyl groups substituted at the nitrogen atom by lower alkyl as groups promoting water-solubility: C.I. Acid Red 219; C.I. Acid Blue 166; C.I. Acid Yellow 116; C.I. Acid Orange 88; C.I. Acid Red 211; C.I. Acid Violet 70; C.I. Acid Blue 171; C.I. Acid Blue 168; C.I. Acid Black 60; C.I. Acid Red 300; C.I. Acid Brown 252;

(c) Monoazo dyestuffs containing an o-areno-oxymethylene-sulfonyl group: C.I. Acid Violet 96; C.I. Acid Blue 200; C.I. Acid Blue 199.

The polyglycol ether used in Example 1 is produced as follows:

92 parts of N-stearyldiethylenetriamine produced by known methods from sulfatized stearyl alcohol and diethylenetriamine, are melted by heating to 70–80°. A solution of 2.3 parts of sodium in 100 parts of alcohol is then added to the reaction mixture. After mixing well, the alcohol is distilled off and 990 parts of ethylene oxide is introduced into the melt at a temperature of 110–120°. On cooling, the reaction mixture solidifies into an almost colorless mass. The product dissolves well in water and foams very little in aqueous solution.

EXAMPLE 2

100 kg. of nylon 6 velour are dyed on the perforated beam of a high temperature beam dyeing machine described in Example 1 in a liquor containing 0.6 kg. of the polyglycol ether used in Example 1; 0.6 kg. of hexamethylenetetramine and about 1 kg. of aqueous 40%-acetic acid in 1500 liters of water. The liquor is circulated in the closed machine for 10 minutes at room temperature and then the mixture of 3 kg. of the brown, mixed, monosulfonated dyestuff chromium complex obtained from 1-phenyl - 3 - methyl - 4 - (2'-hydroxy-5'-sulfophenylazo)-5-pyrazolone and 1-(2'-hydroxy-5'-phenylazophenyl-azo)-2-hydroxynaphthalene with 15 liters of hot water is pumped in. The liquor is circulated for 10 minutes at room temperature, the pressure is brought to 2 to 4 atmospheres excess pressure by a pressure pump, the temperature is gradually and evenly raised within 30 minutes to 100° and dyeing is performed for 40 minutes at this temperature. The liquor is then cooled, excess pressure is removed and the dyed goods are rinsed first warm and then cold. Deep brown, very evenly dyed, wet-fast and light-fast goods are obtained.

When, in this example, analogous, so-called mixed dyestuff-chromium complexes are used, the two co-ordinated azo dyestuffs of which contain open sole sulfonic acid group, e.g. C.I. Acid Blue 184 and C.I. Acid Black 132, light- and wet-fast, very evenly dyed polyamide articles are also obtained.

EXAMPLE 3

In the dyeing machine described in Example 1, 100 kg. of nylon 6 fabric are dyed on the perforated beam in 1500 liters of water containing 1 kg. of polyglycol ether from monostearyl diethylenetriamine, 2 mols of styrene oxide, 100 mols of ethylene oxide, 5 mols of propylene oxide, 0.5 kg. of hexamethylenetetramine and 1.0 kg. of 40%-acetic acid. The liquor is first circulated for 10 minutes at room temperature, 2 to 4 atmospheres excess pressure being applied by an additional pump. Then the mixture of 1.5 kg. of the orange dyestuff chromium complex, produced by adding 2-hydroxybenzene-1-carboxylic acid-5-sulfonic acid phenylamide to the monoazo dyestuff metallized in a ratio of 1 chromium atom per 1-(3'chlorophenyl)-3-methyl-4-(2'-hydroxy-5'-sulfamido-phenyl)-azo-5-pyrazolone, with 15 liters of hot water is then drawn in. The liquor is first circulated for 10 minutes at room temperature and then, in a closed vessel, it is heated up within 40 minutes to 120°. Dyeing is performed for 25 minutes at this temperature. After cooling, the dyeing is rinsed with warm and then cold water. A very level, light- and wet-fast orange dyeing is obtained.

The polyglycol ether used in Example 3 is produced as follows:

92 parts of N-stearyldiethylenetriamine are melted by heating to 70–80°. 62 parts of styrene oxide are then added to the melt and the whole is heated while stirring

at 120°. Heat is then generated and the temperature of the reaction mixture rises to 186°. After cooling to 140–150° the mixture is stirred for about 5 hours at this temperature. Analysis shows that the reaction product obtained is N_1-stearyl-N_2, N_3-bis-(β-phenyl-hydroxyethyl)-diethylenetriamine. A solution of 2.3 parts of sodium in 100 parts of alcohol is then added to the reaction mixture. After mixing well, the alcohol is distilled off and first 60 parts of propylene oxide and then 1100 parts of ethylene oxide are introduced into the melt at a temperature of 110–120°. On cooling, the reaction mixture solidifies into an almost colorless mass. The product dissolves well in water and foams very little in aqueous solution.

EXAMPLE 4

In a high temperature beam dyeing machine, 100 kg. of nylon 6 taffeta are dyed on the beam with a solution of 1 kg. of polyglycol ether from oleylethylenediamine, 1 mol of styrene oxide and 50 ml. of ethylene oxide, 0.8 kg. of hexamethylenetetramine and 2 liters of 40% H_2SO_4 in 1500 liters of water. After bringing the pressure to 2 to 4 atmospheres excess pressure, the liquor is circulated for 10 minutes at room temperature, then the mixture of 2 kg. of the chromium-containing monoazo dyestuff 1-(2′ - hydroxy - 4′ - nitrophenylazo) - 2 - (2″ - carboxy-4″ - sulfamidophenylamino) - naphthalene containing 1 chromium atom and 1 mol of 8-hydroxyquinoline bound in complex linkage, with 15 liters of hot water is added, the liquor is circulated first for 10 minutes at room temperature then, in a closed vessel, it is heated to 120° within 30 minutes and then kept at this temperature for 20 minutes. It is then cooled, the goods are rinsed, after removal of the liquor, with warm and cold water.

A very level, light- and wet-fast green dyeing is obtained.

Dyeings having similar properties are obtained if in this example, the dyestuff disclosed is replaced by the similarly constructed commercial brand C.I. Acid Green 57.

Light-fast, level, pure blue dyeings are obtained also if, with otherwise the same procedure, in the above example 0.5 to 2 kg., depending on the desired depth of shade of a formazane dyestuff containing copper in a ratio of 1:1, (2′ - hydroxy - 5′ - sulfoethylanilide - 4″ - sulfonic acid phenylazo) - (2 - carboxyphenylazo) - phenyl - methane, (2′ - hydroxy - 5′ - m - sulfamidophenylsulfonylphenylazo) - (2 - carboxynaphthyl - (3) - azo) - phenylmethane or -(2′ - hydroxy - 4′ - sulfamido - phenylazo) - (5 - chloro-2-carboxyphenylazo)-phenylmethane is used instead of the dyestuff disclosed.

77.5 parts of N-oleylethylene diamine obtained by condensing oleyl sulfonate with ethylene diamine are reacted at 140–150° with 30 parts of styrene oxide. The mixture is stirred for about 4 hours at this temperature, then 1 part of sodium ethylate is added and then 550 parts of ethylene oxide are added at 110–120°. The reaction is complete after a short time and the product solidifies on cooling.

EXAMPLE 5

In a high temperature beam dyeing machine fitted with a circulation pump, 100 kg. of nylon 6 shirting are dyed under the conditions described in Example 1 on the perforated beam by the method described in the previous examples. A liquor consisting of 2 kg. of polyglycol ether from stearylamine, 1 mol of styrene oxide and 70 mols of ethylene oxide, 0.5 kg. of hexamethylenetetramine and 1 kg. of 40%-acetic acid in 1500 liters of water is used. The goods are dyed with 3 kg. the disazo dyestuff produced from diazotized 3-aminobenzene-1-sulfonic acid-4′-cresol ester sulfonic acid, coupling with the technical mixture of 1-amino-naphthalene-6- and -7- sulfonic acid, diazotizing the aminoazo dyestuff and again coupling with 1-(4′ - methylphenylamino) - naphthalene - 8 - sulfonic acid, by first pre-treating the goods for 10 minutes in the liquor containing the auxiliaries, then adding the mixture of the dyestuff with 15 liters of hot water circulating the liquor in a closed apparatus while heating to 120° within 45 minutes and further treating for 30 minutes at this liquor temperature. The liquor is then cooled to under 100°, removed and the dyed goods are rinsed with warm and cold water. A very level navy blue dyeing is obtained.

Level dyeings having good wet-fastness properties are also obtained if, instead of the neutral to weakly acid drawing dyestuff mentioned above, commercial brands are used which also contain the phenylsulfonic acid phenol ester groups and/or bis-arylamine groups which increase the affinity to wool, for example, on C.I. Acid Red 119, C.I. Acid Yellow 79, C.I. Acid Orange 94, C.I. Acid Red 168.

The polyglycolether used in combination with hexamethylenetetramine as the dye assistant in Example 5, is produced as follows:

67.5 parts of N-stearylamine are melted by heating to 70°. 30 parts of styrene oxide dissolved in toluene are added dropwise to the melt within about 10 minutes. The mixture is then slowly heated to 110°. At this temperature, heat is generated to about 150°. On completion of the reaction, the temperature is kept at 140–150° by warming for about 4 hours. A brown wax is formed which gradually solidifies in the cold.

The resulting N-stearylamino-2-phenylethanol mass obtained as described above is dissolved in 50 parts of alcohol in which 1 part of sodium has been dissolved. After thoroughly mixing, the alcohol is distilled off, the mixture is heated to 120–130° and then ethylene oxide is introduced until the increase in weight of the reaction product is 775 parts. The reaction product obtained solidifies on cooling and then completely dissolves in water.

EXAMPLE 6

100 kg. of nylon 6 fabric are dyed on the beam in a dyeing machine described in Example 1 by pre-treating the goods for 10 minutes at room temperature with the solution of 1 kg. of the known polyglycol ether obtained by condensing a technical mixture of cetyl and oleyl alcohol with ethylene oxide, which product possesses 50 ether groups, 0.8 kg. of hexamethylenetetramine and 0.8 kg. of 40%-acetic acid in 1700 liters of water. The pressure is then raised to 3 atmospheres excess pressure, and aqueous solution of 1.5 kg. of sodium salt of 1,4-bis-(2,6-dimethyl - 4 - phenoxyphenylamino)-anthraquinone disulfonic acid is added and, while circulating the liquor well, the tempearture is raised to 120° within 45 minutes and kept at this temperature for 25 minutes. The temperature is then cooled to under 100°, the liquor is removed and the dyed goods are rinsed with warm and cold water.

A very level, strongly colored, wet-fast blue dyeing is obtained.

Dyeings having similar properties are obtained if, instead of the neutral to weakly acid drawing acid anthraquinone dyestuff described in the example, the similarly constructed commercial brands; C.I. Acid Blue 226; C.I. Acid Green 59; C.I. Acid Green 69.

EXAMPLE 7

100 kg. of nylon 6 knitted articles (tricot) are dyed in a modern type winch. The ends of the goods are sewn together and drawn through the liquor over a round or oval winch continuously. The goods are treated at room temperature for 10 minutes in a solution of 0.6 kg. of polyglycol ether from octadecyldiethylenetriamine, 2 mols of styrene oxide and 100 mols of ethylene oxide and also 0.35 kg. of hexamethylenetetramine and 0.6 kg. of 40%-acetic acid in 1300 liters of water. The mixture of 1%-copper-containing formazane dyestuff [5-sulpho-ethylanilide - 4′ - sulfonic acid - 2 - hydroxyphenylazo] - [2-carboxyphenylazo]-phenylmethane containing 1 dyestuff molecule to 1 copper atom and of 2% disazo dyestuff obtained from tetrazotized 1,1-bis-[4′-(2″-amino-benzenesulfonyloxy)phenyl]-cyclohexane coupled with 2 equiva-

lents of 1-(2'-chloro-5-sulfophenyl)-3-methyl-5-amino-pyrazole, with 15 liters of hot water is added. The liquor is brought to the boil within 40 minutes while circulating the goods well and then dyeing is continued for 45 minutes at the boil. The goods are then rinsed warm and cold.

A very level, full, light-fast green dyeing is obtained.

Similar level dyeings are obtained if, instead of the formazine dyestuff used above, similar copper-containing dyestuffs are used which, instead of a sulfonic acid group, contain sulfamide groups as substituents promoting water-insolubility. Instead of the disazo dyestuff used above, similarly constructed commercial dyestuffs such as C.I. Acid Yellow 79 can be used.

The polyglycol ether used in Example 7 is produced as follows:

92 parts of N-stearyldiethylenetriamine are melted by heating to 70–80°. 62 parts of styrene oxide are then added to the melt and the whole is heated while stirring at 120°. Heat is then generated and the temperature of the reaction mixture rises to 186°. After cooling to 140–150° the mixture is stirred for about 5 hours at this temperature. Analysis shows that the reaction product obtained is N_1-stearyl-N_2,N_3-bis-(β-phenyl-hydroxyethyl)-diethylenetriamine. A solution of 2.3 parts of sodium in 100 parts of alcohol is then added to the reaction mixture. After mixing well, the alcohol is distilled off and 1100 parts of ethylene oxide are introduced into the melt at a temperature of 110–120°. On cooling, the reaction mixture solidifies into an almost colorless mass. The product dissolves well in water and foams very little in aqueous solution.

We claim:

1. A process for dyeing of synthetic polyamide fiber textile material, comprising beam-dyeing, the said material at a temperature of 100 to 130° C. with an aqueous dyestuff preparation which contains:

(a) as coloring agent, a neutral- to weakly acid-drawing anionic wool dyestuff selected from the chromium and cobalt complexes of o,o'-dihydroxy -mono-azo, -disazo and -azomethine dyestuffs, of o-hydroxy-o'-carboxy mono- and dis-azo dyestuffs, of o-hydroxy-o'-amino mono- and dis-azo dyestuffs which, per heavy metal atom, contain two identical or different dyestuffs bound in complex linkage, and contain a group promoting water-solubility which is selected from the group consisting of a lower alkylsulfonyl group, a sulfamyl group or an acylamido group, and is free from or contains, in the case of said dyestuff being a 2:1 complex consisting of a monosulfonated and an unsulfonated basic dyestuff bound in complex linkage to a chromium or cobalt atom, a salt-forming group which dissociates acid;

(b) a non-ionogenic surfactant ether, which is the condensation product obtained by reacting 1 mol of a polyamine of the general formula:

$$L—NH—A(X—A)_m—NH_2$$

wherein:

L represents a lipophilic alkyl or alkenyl radical having 16–18 carbon atoms,

A represents an alkenylene radical selected from the group consisting of $—CH_2—CH_2—$ and

$$—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—$$

radicals,

X represents a member selected from the group consisting of —NH— and —O—, and

m represents one of the numbers 0 to 2,

first with 1 mol of styrene oxide at a temperature of about 100 to 200° C., and then reacting the resulting intermediate in any order desired with 50 to 150 mols of ethylene oxide and 0 to 2 mols of styrene oxide of propylene oxide, at a temperature of about 80 to 200° C.,

(c) hexamethylenetetramine,

(d) the pH of said preparation at the beginning of dyeing being less than 7.5 but not less than 3; the weight ratio of (b) to (c) being in the range of from about 4:1 to 1:4.

2. A process according to claim 1 wherein the pH value of the dyestuff preparation is adjusted to the aforesaid range by addition of a lower aliphatic carboxylic acid.

3. A process as described in claim 1, wherein said ether defined under (b) is a polyaminoether obtained by reacting 1 mol of the polyamine of the general formula:

$$\text{Octadecyl-NH—CH}_2\text{—CH}_2\text{—(NH—CH}_2\text{—CH}_2)_m\text{—NH}_2$$

wherein *m* represents one of the numbers 0 to 2,

first with 1 to 2 mols of styrene oxide and then with 70 to 100 mols of ethylene oxide, and the weight ratio of (b):(c) ranges from about 3:1 to 1:3.

4. A process as described in claim 1, wherein said surfactant ether defined under (b) is the polyglycol ether obtained from monostearyl diethylenetriamine, 2 mols of styrene oxide, 100 mols of ethylene oxide and 5 mols of propylene oxide.

5. A process as described in claim 1, wherein said surfactant ether defined under (b) is the polyglycolether from oleylethylenediamine, 1 mol of styrene oxide and 50 mols of ethylene oxide.

6. A process as described in claim 1, wherein said surfactant ether defined under (b) is the polyglycol ether from stearylamine, 1 mol of styrene oxide and 70 mols of ethylene oxide.

7. A process as described in claim 1, wherein said surfactant ether defined under (b) is the polyglycol ether from octadecyldiethylenetriamine, 2 mols of styrene oxide and 100 mols of ethylene oxide.

8. A process for the dyeing of synthetic polyamide fiber textile material, comprising beam dyeing, the said material at a temperature of 100 to 130° C. with an aqueous dyestuff preparation which contains:

(a) a dyestuff selected from the group consisting of copper complexes of metallizable disazo dyestuffs of the formazane series; unmetallized disazo dyestuffs containing sulfonic acid groups, and 4,4'-bis-(4-amino - 3 - sulfo - anthraquinonyl - 1 - amino)-diphenylalkane dyestuffs:

(b) a non-ionogenic surfactant ether, which is the condensation product obtained by reacting 1 mol of a polyamine of the general formula:

$$L—NH—A(X—A)_m—NH_2$$

wherein:

L represents a lipophilic alkyl or alkenyl radical having 16–18 carbon atoms,

A represents an alkylene radical selected from the group consisting of $—CH_2—CH_2—$ and

$$—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—$$

radicals,

X represents a member selected from the group consisting of —NH— and —O—, and

m represents one of the numbers 0 to 2,

first with 1 mol of styrene oxide at a temperature of about 100 to 200° C., and then reacting the resulting intermediate in any order desired with 50 to 150 mols of ethylene oxide and 0 to 2 mols of styrene oxide of propylene oxide, at a temperature of about 80 to 200° C.,

(c) hexamethylenetetramine,

(d) the pH of said preparation at the beginning of dyeing being less than 7.5 but not less than about 3; the weight ratio of (b) to (c) being in the range of from about 4:1 to 1:4.

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