United States Patent Office

3,097,043
Patented July 9, 1963

3,097,043

NEW DYEING PROCESS

Walter Percival Mills, Manchester, England, assignor to Imperial Chemical Industries Limited, Millbank, London, England, a corporation of Great Britain

No Drawing. Filed Nov. 4, 1959, Ser. No. 850,785
Claims priority, application Great Britain Nov. 7, 1958
6 Claims. (Cl. 8—55)

This invention relates to a dyeing process and more particularly it relates to a process for dyeing synthetic polymeric textile materials.

It is known that synthetic polymeric textile materials can be dyed with disperse dyestuffs which are free from sulphonic acid and carboxylic acid groups and which contain at least one reactive halogen atom or other reactive group which is capable of reacting with the synthetic polymeric textile material so that the said disperse dyestuff is fixed to the synthetic polymeric textile material by a chemical bond, whereby dyeings are obtained which have excellent fastness to washing.

It has now been found that the fixation of such disperse reactive dyestuffs to the synthetic polymeric textile materials is low when the dyestuffs are applied from a dyebath the pH of which is less than 7 but as the pH rises fixation of the dyestuff rapidly increases. However at pH's above 7 the uptake of the dyestuff onto the synthetic polymeric textile material is uneven and level dyeings are not obtained. It has now been found that this disadvantage can be overcome by commencing the dyeing of the synthetic polymeric textile material with the disperse reactive dyestuffs at a pH less than 7 and subsequently raising the pH during the dyeing operation, whereby level dyeings are obtained possessing excellent fastness to washing.

According to the invention therefore there is provided an improved process for dyeing synthetic polymeric textile materials with disperse reactive dyestuffs, as hereinafter defined, which comprises dyeing the synthetic polymeric textile material with an aqueous dispersion of the said dyestuff at a pH less than 7 and subsequently raising the pH during the dyeing process.

The process of the invention may be conveniently carried out by immersing the synthetic polymeric textile material in an aqueous dispersion of the disperse reactive dyestuff containing an acid or an acid-salt so that the pH of the aqueous dispersion is less than 7 and is preferably between 3 and 5, heating the dyebath for a period at a suitable temperature, for example at a temperature between 90° to 100° C., adding an alkali or an alkaline salt to raise the pH of the dyebath, preferably to a pH between 9 and 12, and heating for a further period at a suitable temperature, for example at a temperature between 90° and 100° C. The textile material is then removed from the dyebath, rinsed in water and dried.

If desired the process of the invention may be carried out at temperatures above 100° C., for example at temperatures between 100° and 130° C. under superatmospheric pressure.

Alternatively the process of the invention can be carried out at temperatures below 90° C., for example at temperatures between 70° and 90° C., but, in order that the resulting dyeings shall possess maximum fastness to washing, it is preferred to subsequently subject the dyeing so obtained to a dry heat treatment at a temperature beween 160° and 230° C. This can be conveniently carried out by placing the dyed synthetic polymeric textile materials in contact with a metal cylinder which is maintained at a temperature between 160° and 230° C.

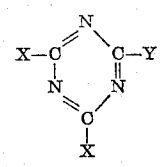
As examples of the acids or acid salts which may be used in the process of the invention there may be mentioned organic acids for example aliphatic organic acids and in particular monobasic lower fatty acids such as acetic acid and formic acid and inorganic acid salts such as sodium dihydrogen phosphate, and as examples of the alkalis or alkaline salts which may be used in the process of the invention there may be mentioned inorganic alkalis and inorganic alkaline salts such as sodium carbonate, sodium hydroxide, trisodium phosphate, barium hydroxide, lithium hydroxide, sodium silicate, potassium carbonate and potassium hydroxide.

If desired mixtures of acids and/or acid salts and/or mixtures of alkalis and/or alkaline salts may be used in the process of the invention.

By the term "disperse reactive dyestuff" there is meant a disperse or water-insoluble dyestuff which is free from sulphonic acid and carboxylic acid groups and which contains at least one reactive halogen atom or other reactive atom or group, that is to say a halogen atom or other group capable of reacting with the synthetic polymeric textile material. Examples of classes of such disperse reactive dyestuffs include water-insoluble dyestuffs containing a 1:3:5-triazinyl radical carrying one or two chlorine or bromine atoms directly attached to the triazine ring, disperse dyestuffs containing a pyrimidyl radical carrying one or two chlorine or bromine atoms directly attached to the pyrimidine ring, disperse dyestuffs containing at least one γ-halogeno-β-hydroxypropylamino group, disperse dyestuffs containing at least one di-(γ-halogeno-β-hydroxypropyl)amino group, disperse dyestuffs containing at least one β-halogenoethylsulphamyl group, disperse dyestuffs containing at least one β-halogenoethoxy group, disperse dyestuffs containing at least one β-halogenothioethane groups, disperse dyestuffs containing at least one γ-halogeno-β-hydroxypropylsulphamyl group, disperse dyestuffs containing at least one chloracylamino group, disperse dyestuffs containing at least one vinylsulphonyl group and disperse dyestuffs containing at least one epoxy propyl group. The disperse dyestuffs in these classes may be for example nitro dyestuffs or dyestuffs of the azo, anthraquinone or phthalocyanine series which are free from sulphonic and carboxylic acid groups.

It is however preferred that the disperse reactive dyestuff contains a monohalogenotriazinylamine group such as a 4-chloro-6-amino-1:3:5-triazin-2-ylamino group, or a γ-halogeno-β-hydroxypropyl group such as a γ-chloro-β-hydroxypropylamino group, or a β-halogenoalkylsulphamyl group such as a β-chloroethylsulphamyl or a β-bromoethylsulphamyl group.

Disperse dyestuffs containing a dichloro or dibromo-1:3:5-triazinyl radical may be obtained by reacting one molecular proportion of a disperse dyestuff containing a primary amino or secondary amino group with one molecular proportion of cyanuric chloride or cyanuric bromide Disperse dyestuffs containing a monochloro- or monobromo-1:3:5-triazinyl radical may be obtained by reacting one molecular proportion of a disperse dyestuff containing a primary amino or secondary amino group with one molecular proportion of a triazine of the formula:



wherein X is a chlorine or bromine atom and Y stands for an alkyl, aryl or amino group or for an organic radical

containing a nitrogen, oxygen or sulphur atom through which it is linked to the triazine ring.

Disperse dyestuffs containing a pyrimidyl radical carrying one or two chlorine or bromine atoms directly attached to the pyrimidine ring may be obtained by interacting substantially equimolecular proportions of a disperse dyestuff containing a primary amino or secondary amino group and a pyrimidine containing at least two chlorine or bromine atoms in the 2, 4, or 6 positions of the pyrimidine ring. As examples of such pyrimidines there may be mentioned 2:4:6-trichloropyrimidine, 2:4 - dibromopyrimidine, 2:4 - dichloro - 6 - methylpyrimidine, 2:4 - dichloro - 6 - methoxypyrimidine, 2:4-dichloro-6-phenylpyrimidine, 2:4-dichloro-6-nitropyrimidine, 2:4-dichloro-6-hydroxypyrimidine, 2:4:6-trichloro-5-nitropyrimidine and 2:4-dichloro-5-nitro-6-methylpyrimidine.

Disperse dyestuffs containing at least one γ-halogeno-β-hydroxypropylsulphamyl or β - halogenoethylsulphamyl group may be obtained by treating a disperse dyestuff containing at least one sulphonchloride group with a γ-halogeno-β-hydroxypropylamine or a β-halogenoethylamine respectively.

Disperse dyestuffs containing at least one β-halogenoethoxy or β-halogenothioethane group may be obtained by treating a disperse dyestuff containing at least one β-hydroxyethoxy or β-hydroxythioethane group with a halogenating agent.

Disperse dyestuffs containing at least one γ-halogeno-β-hydroxypropylamino or di-(γ-halogeno-β-hydroxypropyl)amino group may be obtained by reacting a disperse dyestuff containing one or more primary amino groups with epichlorohydrin and separating the mixture of products so obtained.

Disperse dyestuffs containing a propylepoxy group may be obtained by reacting the corresponding dyestuffs containing a γ-chloro-β-hydroxypropyl group with potassium hydroxide.

Disperse dyestuffs containing a vinylsulphone group may be obtained by treating with an alkali, for example potassium hydroxide, the corresponding dyestuffs containing a β-sulphatoethylsulphonyl group, which may themselves be obtained by sulphating the corresponding dyestuffs containing a β-hydroxyethyl group.

Disperse dyestuffs containing at least one chloracylamino group may be obtained by treating the corresponding dyeustff containing at least one amino group with a chloroacyl chloride such as chloracetyl chloride.

Examples of disperse reactive dyestuffs which may be used in the process of the invention are described in British specifications Nos. 822,948 and 825,377, French specification No. 1,177,851, Belgian specifications Nos. 563,862, 571,741, 571,742 and 571,743, and in United States patent specification No. 2,258,977.

As specific examples of disperse reactive dyestuffs which may be used in the process of the invention there may be mentioned

2-hydroxy-5-methyl-4'-(4'':6''-dichloro-1'':3'':5''-triazin-2''-ylamino)azobenzene,

2-chloro-4-ethanesulphonyl-4'-N-β-hydroxyethyl-N-β-(4'':6''-dichloro-1'':3'':5''-triazin-2''-ylamino)-ethylaminoazobenzene,

4-(4'':6''-dichloro-1'':3'':5''-triazin-2''-ylamino)-2-methylazobenzene,

2-hydroxy-5-methyl-4'-(4'':6''-dibromo-1'':3'':5''-triazin-2''-ylamino)-azobenzene,

2-hydroxy-5-methyl-4'-(4''-chloro-6''-β-hydroxyethylamino-1'':3'':5''-triazin-2''-ylamino)azobenzene,

2-hydroxy-5-methyl-4'-(4''-chloro-6''-anilino-1'':3'':5''-triazin-2''-ylamino)azobenzene,

2-hydroxy-5-methyl-4'-(4''-chloro-6''-amino-1'':3'':5''-triazin-2''-ylamino)azobenzene,

2-chloro-4-ethanesulphonyl-4'-N-β-hydroxyethyl-N-β-(4''-chloro-6''-hydroxy-1'':3'':5''-triazin-2''-ylamino)-ethylaminoazobenzene,

2-hydroxy-5-methyl-4'-(4''-bromo-6''-N:N-di(β-hydroxyethyl)amino-1'':3'':5''-triazin-2''-ylamino)azobenzene,

2-hydroxy-5-methyl-4'-(4''-chloro-6''-phenyl-1'':3'':5''-triazin-2''-ylamino)azobenzene,

4-amino-4'-(4''-chloro-6''-phenoxy-1'':3'':5''-triazin-2''-ylamino)azobenzene,

1-4'-(4'':6''-dichloro-1'':3'':5''-triazin-2''-ylamino)anilinoanthroquinone,

1-4'-(4''chloro-6''-phenoxy-1'':3'':5''-triazin-2''-ylamino)anilinoanthraquinone,

4'-(4''-6''-dichloro-1'':3'':5''-triazin-2''-ylamino)2:4-dinitrodiphenylamine,

4'-(4''-chloro-6''-methoxytriazin-2''-ylamino)-2:4-dinitrodiphenylamine,

3'-(4''-chloro-6''-phenoxy-1'':3'':5''-triazin-2''-ylamino)-2-nitro-4-trifluoromethyldiphenylamine,

2-hydroxy-5-methyl-4'-(4'':6''-dichloro-pyrimidine-2''-ylamino)azobenzene,

4'-nitro-4-N:N-di(γ-chloro-β-hydroxypropyl)aminoazobenzene,

1:4-bis(γ-chloro-β-hydroxypropylamine)anthraquinone,

4'-β-chloroethylsulphamylphenylazo-4-β-hydroxyethylaminonaphthalene,

4-β-chloroethylsulphamyl-2'-methyl-5'-N-ethyl-N-β-hydroxyethylaminoazobenzene,

2-chloro-4-β-chloroethylsulphamyl-2'-methyl-5'-di(beta-hydroxyethyl)aminoazobenzene,

1-methylamino-4-β-chloroethylamino-anthraquinone,

1:4'-(4'':6''-dichloro-1'':3'':5::-triazin-2-ylamino)phenylazo-2-naphthol,

1-amino-2-β-bromoethoxy-4-hydroxyanthraquinone,

1-amino-4-hydroxy-2-β-(β'-chloroethoxy)ethoxyanthraquinoine and

1-amino-4-hydroxy-2-β-(β'-bromoethoxy)ethoxyanthraquinone.

As examples of synthetic polymeric textile materials which may be dyed by the process of the invention there may be mentioned nitrogen-containing synthetic textile materials such as polyamide textile materials for example textile materials comprising polyhexamethyleneadipamide or the polymer of caprolactam, and modified polyacrylonitrile textile materials.

By the process of the invention there are obtained on the synthetic polymeric textile materials level dyeings in a wide range of shades which have excellent fastness to washing and to dry heat treatments.

The invention is illustrated but not limited by the following examples in which the parts and percentages are by weight:

Example 1

1 part of 2-hydroxy-5-methyl-4'-(4''-chloro-6''-di(β-hydroxyethyl)amino-1'':3'':5''-triazin-2''-ylamino)azobenzene is dispersed in 20 parts of water and the dispersion so obtained is added to 4,000 parts of water containing 4 parts of the condensate of ethylene oxide with a fatty alcohol and 8 parts of sodium dihydrogen phosphate. 100 parts of polyhexamethylene adipamide textile material are placed in the dyebath thus obtained which is then heated to 95° C. and maintained at this temperature for 60 minutes. 9.2 parts of sodium carbonate are then added and dyeing is continued for a further hour at a temperature of 95° C. The dyed fabric is then rinsed in water and dried. The polyhexamethyleneadipamide textile material is uniformly colored a yellow shade possessing superior wash and dry heat fasteness properties to polyhexamethyleneadipamide textile material which was dyed as described above except that the sodium carbonate was omitted from the dyebath.

Example 2

1 part of 1:4-di(γ-chloro-β-hydroxypropylamino)anthraquinone is dispersed in 20 parts of water and the dispersion so obtained is added to 4,000 parts of water containing 4 parts of the condensate of ethylene oxide

with a fatty alcohol and 1 part of acetic acid. 100 parts of polymerised caprolactam textile material are placed in the dyebath thus obtained which is heated to 95° C. and maintained at this temperature for 60 minutes. 4 parts of barium hydroxide are then added and dyeing is continued for 1 hour at 95° C. The dyed textile material is finally rinsed in water and dried. The textile material is uniformally dyed a blue shade and the fastness properties to wet and dry heat treatments are substantially better than the same fastness properties of a dyeing obtained as described above except that the 1 part of acetic and 1 part of barium hydroxide were omitted from the dyebath.

Example 3

1 part of 2'-methyl-4-β-chloroethylsulphamyl-4'-N:N-di(β-hydroxyethyl)aminoazobenzene is dispersed in 20 parts of water and the dispersion so obtained is added to 4,000 parts of water containing 4 parts of the condensate of ethylene oxide with a fatty alcohol and 4 parts of acetic acid. 100 parts of polyhexamethyleneadipamide textile material are immersed in the dyebath so obtained which is heated to 95° C. and maintained at this temperature for 45 minutes. 5 parts of sodium hydroxide are then added and dyeing is continued for 1 hour at 95° C. The dyed textile material is then rinsed in cold water and dried. The textile material is dyed a uniform orange shade possessing superior wet and dry heat fastness properties to polyhexamethyleneadipamide textile material which was dyed as described above except that the caustic soda was omitted from the dyebath.

Example 4

In place of the 1 part of 2-hydroxy-5-methyl-4'-(4''-chloro - 6'' - di(β - hydroxyethyl)amino - 1'':3'':5'' - triazin-2''-ylamino)azobenzene used in Example 1 there is used 1 part of 2-methyl-4'-β-chloroethylsulphamyl-4-N-β-hydroxyethylaminoazobenzene. The polyhexamethyleneadipamide textile material is coloured an orange shade possessing excellent wash fastness properties.

Example 5

In place of the 1 part of 2-hydroxy-5-methyl-4'-(4-chloro - 6 - di(β - hydroxyethyl)amino - 1:3:5 - triazin-2-ylamino)azobenzene used in Example 1 there is used 1 part of 1:4-bis(γ-bromo-β-hydroxypropylamino)anthraquinone. The polyhexamethyleneadipamide textile material is coloured a blue shade possessing excellent wash fastness properties.

Example 6

In place of the 1 part of 2-hydroxy-5-methyl-4'-(4''-chloro - 6'' - di(β - hydroxyethyl)amino - 1'':3'':5'' - triazin-2''-yl-amino)azobenzene used in Example 1 there is used 1 part of 2-methyl-2'-chloro-4'-β-chloroethylsulphamyl - 4 - N:N - di(β-hydroxyethyl)aminoazobenzene. The polyhexamethyleneadipamide textile material is coloured a scarlet shade possessing excellent fastness to washing.

Example 7

1 part of 1:4-di-(γ-chloro-β-hydroxypropylamino)anthraquinone is dispersed in 20 parts of water and the dispersion so obtained is added to 4,000 parts of water containing 8 parts of oleyl sodium sulphate and 8 parts of sodium dihydrogen phosphate. 100 parts of "Acrilan," a modified polyacrylonitrile fibre manufactured by the Chemstrand Corporation, are placed in the dyebath thus obtained which is then heated to 95° C. and maintained at this temperature for 60 minutes. 9.2 parts of sodium carbonate are then added and dyeing is continued for a further hour at a temperature of 95° C. The dyed fabric is then rinsed in water and dried. The "Acrilan" is coloured a blue shade possessing excellent fastness to washing.

Example 8

1 part of 1:4-bis(γ-chloro-β-hydroxypropylamino)anthraquinone is dispersed in 20 parts of water and the dispersion is added to 4,000 parts of water containing 4 parts of the condensate of ethylene oxide with a fatty alcohol and 8 parts of a 30% aqueous solution of acetic acid. 100 parts of polyhexamethyleneadipamide textile material are placed in the dyebath thus obtained which is then heated at 70° C. and maintained at this temperature for 30 minutes. A solution of 8 parts of sodium carbonate in 50 parts of water is then added and dyeing is continued for a further 60 minutes at a temperature of 70° C. The fabric is then removed from the dyebath, rinsed in cold water and dried. The dyed polyhexamethyleneadipamide textile material is then placed in contact for 15 seconds with a metal cylinder which is maintained at a temperature of 220° C.

The polyhexamethyleneadipamide textile material is coloured a blue shade possessing superior wash fastness properties to polyhexamethyleneadipamide textile material which was dyed as described above but was not subsequently heated at 220° C.

Example 9

In place of the 1 part of 1:4-bis(γ-chloro-β-hydroxypropylamino)anthraquinone used in Example 8 there is used 1 part of 2-methyl-2'-chloro-4'-β-chloroethylsulphamyl - 4 - N:N - di(β - hydroxyethyl)aminoazobenzene. The polyhexamethyleneadipamide textile material is coloured a scarlet shade possessing superior wash fastness properties to polyhexamethyleneadipamide textile material which was dyed as described above but was not subjected to the heat treatment at 220° C.

Example 10

In place of the 1 part of 1:4-bis(γ-chloro-β-hydroxypropylamino)anthraquinone used in Example 8 there is used 1 part of 2-hydroxy-5-methyl-4'-(4''-chloro-6''-di(β-hydroxyethyl)amino - 1'':3'':5'' - triazin - 2'' - ylamino)-azobenzene. The polyhexamethyleneadipamide textile material is thereby coloured a yellow shade possessing superior wash fastness properties to polyhexamethyleneadipamide textile material which was dyed as described above but was not subjected to the heat treatment at 220° C.

Example 11

In place of the 1 part of 1:4-bis(γ-chloro-β-hydroxypropylamino)anthraquinone used in Example 8 there is used 1 part of 2-methyl-4'-β-chloroethylsulphamyl-4-N:N-di(β-hydroxyethyl)aminoazobenzene.

The polyhexamethyleneadipamide textile material is thereby coloured an orange shade possessing superior wash fastness properties to polyhexamethyleneadipamide textile material which was dyed as described above but was not subjected to the heat treatment at 220° C.

Example 12

In place of the 1 part of 1:4-bis(γ-chloro-β-hydroxypropylamino)anthraquinone used in Example 8 there is used 1 part of 1-β-hydroxyethylamino-4-[2'-chloro-4'-β-chloroethylsulphamylphenylazo]-naphthalene.

The polyhexamethyleneadipamide textile material is thereby coloured a red shade possessing superior wash fastness properties to polyhexamethyleneadipamide textile material which was dyed as described above but was not subjected to the heat treatment at 220° C.

Example 13

In place of the polyhexamethyleneadipamide textile material used in Example 8 there is used a textile material comprising polymerised caprolactam, and instead of heating the dyed textile material at 220° C. for 15 seconds, the dyed textile material is heated at 190° C. for 45 seconds whereby the textile material is coloured a

blue shade possessing superior wash fastness properties to the polymerised caprolactam textile material which was dyed as described above but was not subjected to the heat treatment at 190° C.

What I claim is:

1. Process for dyeing nitrogen-containing synthetic polymeric textile materials selected from the class consisting of synthetic linear polyamides and modified polyacrylonitrile textile materials, which process comprises dyeing said synthetic polymeric textile material with an aqueous dispersion of a disperse reactive dyestuff and a member selected from the group consisting of an acid and acid salt, and having a pH in the range of between about 3 and 5, and subsequently, during the dyeing process, adding to said dispersion a member selected from the group consisting of an alkali and alkaline salt, to raise the pH thereof to within the range of between about 9 and 12.

2. Process as claimed in claim 1 wherein the dyeing is carried out at a temperature between 90° and 100° C.

3. Process as claimed in claim 1 wherein the dyeing is carried out at a temperature between 100° and 130° C., under superatmospheric pressure.

4. Process is claimed in claim 1 wherein the nitrogen-containing synthetic polymeric textile material is a polyamide textile material.

5. Process as claimed in claim 1 wherein the dyeing is carried out at a temperature between 70° and 90° C.

6. Process as claimed in claim 5 wherein the dyed textile material is subsequently given a dry heat treatment at a temperature between 160° and 230° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,895,785	Alsberg et al.	July 21, 1959
2,900,218	Gray	Aug. 18, 1959
2,903,442	Riat	Sept .8, 1959
2,914,531	Staeuble	Nov. 24, 1959
2,944,870	Atkinson et al.	July 12, 1960
2,944,871	Atkinson et al.	July 12, 1960
2,952,506	Dellis	Sept. 13, 1960

OTHER REFERENCES

Schlaeppi: Amer. Dyest. Rep., June 2, 1958, p. 377, 8–54.2.