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3,545,910

PROCESS FOR DYEING MIXTURES OF CELLULOSIC AND POLYESTER FIBERS WITH REACTIVE AND DISPERSE DYE STUFFS

Sien Ling Ong, Steinheim am Main, Germany, assignor to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruning, Frankfurt am Main, Germany
No Drawing. Filed Feb. 21, 1967, Ser. No. 617,477
Claims priority, application Germany, Feb. 23, 1966, F 49,498

Int. Cl. D06p 3/82

U.S. Cl. 8-21

8 Claims

ABSTRACT OF THE DISCLOSURE

A process for dyeing mixtures of cellulosic fibers and high molecular weight linear polyester fibers which comprises using an aqueous dyebath which contains both reactive and disperse dyestuffs, an alkaline compound to give the bath an initial alkaline pH and an acid donor which reacts with water, when heated, to split off a hydrogen halide and thereby reduce the pH of the bath during the dyeing process. The reactive and disperse dyestuffs used are conventional. The alkaline compound may be, for example, an alkali metal carbonate, bicarbonate, triphosphate or hydroxide. The acid donor may be any of a wide variety of halogenated compounds, typically salts, amides or anilides of mono- and di-halogenated acetic and propionic acids, e.g., chloracetamide. The bath is heated to a temperature of, e.g., 125° C. to cause the acid donor to split off the hydrogen halide and reduce the pH of the bath. Uniform dyeing of both types of fibers is achieved.

It is known that reactive dyestuffs can be fixed in an alkaline medium. For example a medium prepared using alkali metal hydroxides or alkali metal salts of weak organic acids, on cellulosic fibrous materials. In practice, this fixation in the dyeing or printing with reactive dyestuffs is carried out with the use of an excess of alkaline substances or of substances which have an alkaline action. When alkali metal hydroxides or alkali metal carbonates are used, the pH-value remains constant during the whole fixing process. When alkali metal bicarbonates are used, the pH-value strongly rises shortly after the beginning of the fixing process and then reaches a limit value which remains constant until completion of the fixing process.

The dyeing with reaction dyestuffs involves difficulties when mixtures of cellulosic fibers with, for example polyester fibers are to be dyed simultaneously with reactive and disperse dyestuffs, because the dyeing conditions for these two types of dyestuffs are different. Disperse dyestuffs require longer fixing periods and the action of higher temperatures. The dyeing with disperse dyestuffs is generally carried out at a neutral to weakly acidic pH-value, whereas an alkaline pH-value is required for the fixing of reactive dyestuffs. Furthermore, in the case of reactive dyestuffs, a prolonged treatment with alkaline substances at elevated temperatures strongly reduces the yield of dyestuff being fixed on the fibers, which reaction is due to a splitting of the dyestuff-fiber linkage.

Furthermore, with the alkaline agents commonly used in dyeing, for example, alkali metal bicarbonates, alkali metal carbonates or alkali metal hydroxides, it is not possible to fix reactive dyestuffs on cellulose according to the exhaust process at those elevated temperatures of above about 95° C. which are required for the dyeing of the polyester fiber portion with disperse dyestuffs. Finally, most of the disperse dyestuffs are chemically modified by a prolonged action of alkaline substances at elevated tem-

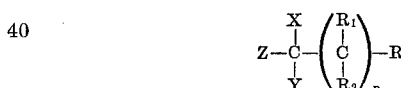
peratures, which results in a deterioration of the properties of fastness and of the shade.

Now, we have found that the above-described disadvantages can be avoided and that mixtures of cellulosic fibers with fibrous materials made of linear polyesters can be dyed simultaneously with reactive and disperse dyestuffs according to the exhaust method at temperatures of above 100° C., by using dyebaths which contain, in addition to the above-mentioned dyestuffs, alkaline substances and halogenated organic compounds which act as acid donors by reacting with water, preferably at elevated temperature, to split off hydrogen halide and, if desired or required, the carriers commonly used in the dyeing of polyester fibers.

The addition of halogenated organic compounds, which act as acid donors, to the dyebaths according to the present invention results in a reduction of the pH-value during the fixing process. This not only permits the use of reactive dyestuffs in the exhaust process at temperatures of above 100° C., but also considerably reduces the risk of a breaking of the fiber-dyestuff linkage. Furthermore, in the process of the present invention, the disperse dyestuffs do not undergo chemical modification.

The quantity of halogenated organic compounds which act as acid donors and which are to be added to dyebaths depends above all on the quantity of alkaline substances contained in the baths. If this content of alkaline substances is in the usual range, the halogenated organic compounds are generally added in quantities ranging from about 0.4 to 40 g./l. of dyebath. The quantity of halogenated organic compounds is so chosen that, after splitting off of hydrogen halide, a pH-value of below about 8.0 is obtained.

As halogenated organic compounds, which act as acid donors in the process of the present invention, there may be used especially aliphatic, cycloaliphatic or heterocyclic compounds containing one or more halogen atoms and which correspond to the following general formula



In the above formula

X represents chlorine, bromine, iodine or hydroxyl,
Y represents hydrogen, hydroxyl, alkyl, phenyl, chlorine, bromine or iodine,
Z represents hydrogen, alkyl, phenyl or the radical



n represents 0 or an integer from 1-5,

R₁ represents hydrogen, hydroxyl, chlorine, bromine or iodine, or alkyl or phenyl radicals which can contain hydrosolubilising groups such, for example, as —COOH, —SO₃H or —OH, at least one of X, Y and R₁ being halogen,

R₂ represents hydrogen or alkyl or phenyl radicals which may contain hydrosolubilising groups such, for example as —COOH, —PO₃H₂, —SO₃H or —OH,

R represents hydrogen, —OH, —CHO, —COOH, —SO₃H, —CONH₂, —CONH-alkyl, —CN, CON-(alkyl)₂, —SO₂NH₂, —SO₂NH-alkyl, —SO₂N(alkyl)₂,



or a radical of the formula



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wherein A represents —O—, —CO—, —SO—, —SO₂—, —CONH—, —SO₂NH—, —CON(alkyl)—, —CON(phenyl)—, —SO₂N(alkyl)— or —SO₂N(phenyl)—; the alkyl and phenyl radicals may contain hydrosolubilising groups. Furthermore, R may represent a radical A which is bound with C₁, over the group



which in the general formula stands instead of Z, thus forming a ring system.

As alkyl radicals in the above general formula, there are to be understood preferably low molecular weight alkyl radicals containing about 1-6 carbon atoms. The phenyl radicals may carry additional substituents, for example, low molecular weight alkyl radicals.

As suitable halogenated organic compounds which in an aqueous medium, preferably at elevated temperatures, react with water under splitting off of hydrogen halide, there may be mentioned, by way of example:

chloroacetic acid
3-chloro-propinoic acid
phenyl-chloroacetic acid
3-chloro-propionic acid nitrile
ethylene-chlorhydrin
1,3-dichloro-propanol-(2)
1-chloro-propanol-(2)
3-chloro-propylene oxide
2-chloro-ethane-sulfonic acid
1-chloro-propanol-(2)-sulfonic acid -(3)
3-chloro-propane-diol-(1,2)
1-chloro-caprolactam
2-trichloromethyl-propanol-(2)
3-chloro-propionaldehyde
dichloroacetic acid

and the alkali metal salts, especially the sodium or potassium salts, amides or anilides of the aforementioned acids.

According to the process of the present invention, the halogenated organic compounds which act as acid donors are added to the dyebaths in such quantities that after the splitting off of hydrogen halide a pH-value of below 8.0, suitably below 7.5 and preferably in the range of between 4 and 6 is obtained. The quantity of halogenated organic compounds to be added depends thus on the quantity of alkaline substances used and therewith indirectly on the quantity of reactive dyestuffs used. Generally, the quantity of halogenated organic compounds to be added to the dyebath will be in the range of about 0.1 to 10 parts by weight, especially 1-5 parts by weight per one part by weight of reactive dyestuff, provided that the pH-value of the bath is in the range which is usual in the dyeing with reactive dyestuffs.

As alkaline substances which are required for the fixation of the reactive dyestuffs, there may be used organic compounds having an alkaline action or, advantageously, inorganic alkaline substances such as sodium carbonate, sodium bicarbonate, sodium triphosphate, sodium hydroxide, the corresponding potassium compounds or mixtures of these alkaline substances. The alkaline substances are used in such quantities that the dyebaths have a pH-value of above 8.0, preferably in the range of 9-12. Generally, the alkaline substances are added to the dyebaths in quantities of about 0.1-10 g./l.

As disperse dyestuffs, there may be used the dyestuffs generally known as suitable for the dyeing of fibrous materials of linear polyesters, for example the dyestuffs of the azo or anthraquinone series.

As reactive dyestuffs, there may be used organic dyestuffs which contain at least one group capable of re-

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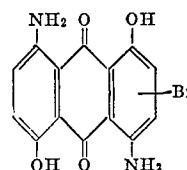
acting with the cellulose fiber or a precursor to such a group or also a substituent which is capable of reacting with the cellulose fiber. As parent component of the organic dyestuffs, there are especially suitable those of the series of the anthraquinone, azo and phthalocyanine dyestuffs; the azo and phthalocyanine dyestuffs may be metal-free or metallised. As reactive groups or as precursors which form such reactive groups in an alkaline medium, there may be mentioned, for example, the epoxy group, ethylene imide groups, the vinyl radical in a vinyl-sulfone group or in the acrylic acid group, furthermore the β -sulfoethyl-sulfonyl group. As reactive substituents, there enter into consideration substituents which can easily be split off and leave behind an electrophilic radical; as examples of such substituents, there may be mentioned halogen atoms in the following ring systems: quinoxaline, triazine, pyrimidine, phthalazine and pyridazone.

The carriers which may be used simultaneously may be those commonly used in the dyeing of polyester fibers, for example o-phenyl-phenol, p-phenyl-phenol, benzoic acid alkyl esters, salicylic acid alkyl esters and similar compounds. Other suitable carriers are, for example, those described in the papers published in "Melliand Textilberichte" (1961), page 1275, and (1960), page 198, as well as in "Textil-Praxis" (1957) pages 383-384, and in the ICI-Technical Report "The Dyeing of Terylene," part I, dated Dec. 11, 1947.

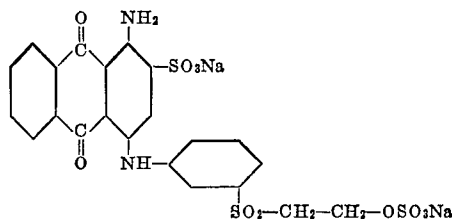
The following examples illustrate the invention but they are not intended to limit it thereto:

EXAMPLE 1

5 grams of a mixed yarn of 70 parts of polyester fibers and 30 parts of staple fibers were dyed for 1½ hours, at a goods-to-liquor ratio of 1:20, in a closed dyeing apparatus, at 125° C., in a dye bath containing 1%, referred to the weight of the goods, of the disperse dyestuff of the formula



having the form and composition usual in commerce, and 5% of the reactive dyestuff of the formula



having the form and composition usual in commerce, and

1 gram/liter of sodium carbonate,
4 grams/liter of chloroacetamide, and
12.5 grams/liter of sodium sulfate.

After dyeing, the goods were rinsed hot and soaped with 1 gram/liter of an anion-active or non-ionic detergent, rinsed again and dried. A uniform brilliant blue dyeing was obtained.

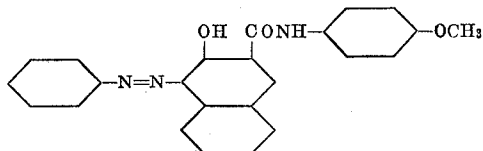
EXAMPLE 2

5 grams of a mixed fabric of 67 parts of polyester fibers and 33 parts of cotton were dyed for 1½ hours

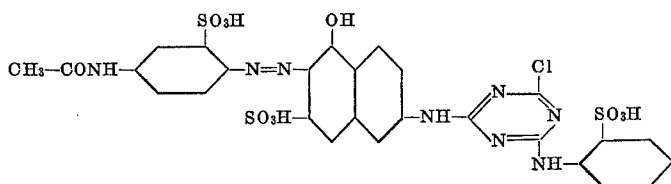
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at a goods-to-liquor ratio of 1:40, in a boiling dyebath containing, referred to the weight of the goods:

1.5% of the disperse dyestuff of the formula



having the form and composition usual in commerce, 1.5% of the reactive dyestuff of the formula



having the form and composition usual in commerce, and 1 gram/liter of sodium carbonate, 4 grams/liter of chloroacetamide, 25 grams/liter of a carrier on the basis of methylnaphthalene in the form usual in commerce, and 12.5 grams/liter of sodium sulfate.

After dyeing, the goods were rinsed, soaped and dried as usual. Both types of fibers of the fabric were dyed a brilliant red shade.

I claim:

1. In a process for dyeing mixtures of cellulosic and high molecular weight linear polyester fibers according to an exhaust method in a single bath containing both reactive and disperse dyestuffs and an inorganic alkaline substance to render said bath alkaline, the improvement which comprises incorporating in said bath an acid donor which is a halogenated organic compound that at an elevated temperature reacts with water to split off a hydrogen halide, and heating said bath to a temperature above 100° C. to cause said acid donor to produce hydrogen halide to reduce the pH of said bath to a value below about 8 during the dyeing operation, said acid donor being selected from monochloroacetic acid, 3-chloro-propionic acid, phenyl-chloroacetic acid, 3-chloro-propionic acid nitrile, ethylene-chlorohydrin, 1,3-dichloro - propanol-(2), 1-chloro-propanol-(2), 3-chloro-propylene oxide, 2-chloro-ethane-sulfonic acid, 1-chloro-propanol-(2)-sulfonic acid-(3), 3-chloro-propane-diol-(1,2), 1-chloro-caprolactam, 2-trichloromethyl-propanol-(2), and 3-chloro-propionaldehyde, and the sodium and

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potassium salts and unsubstituted amides of the aforementioned acids.

2. A process as claimed in claim 1, wherein the halogenated organic compound is added in a quantity such that during the dyeing process the pH-value of the bath is adjusted to below 7.5.

3. A process as claimed in claim 2, wherein the halogenated organic compound is added in a quantity such that during the dyeing process the pH-value of the bath is adjusted to a range of between 4 and 6.

4. A process as claimed in claim 1, wherein the alkaline substance is added to the dyebath in a quantity such that the pH-value of the bath is initially above 8.

5. A process as claimed in claim 4, wherein the alkaline substance is added in a quantity that the pH-value of the bath is initially within the range from 9 to 12.

6. A process as claimed in claim 1, wherein the alkaline substance used is sodium carbonate, sodium bicarbonate, sodium triphosphate, sodium hydroxide, the corresponding potassium salts or mixtures of these alkaline substances.

7. A process according to claim 1 in which the acid donor is chloroacetamide.

8. A process as claimed in claim 1 and wherein the bath contains a carrier selected from o-phenyl-phenol, p-phenyl-phenol, a benzoic acid alkyl ester of a salicylic acid alkyl ester.

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DONALD LEVY, Primary Examiner

U.S. Cl. X.R.

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