METHOD OF DYING TEXTILE FIBERS WITH AN ANIONIC DYE STUFF IN THE PRESENCE OF A QUATERNARY AMMONIUM SALT

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The portion of the term of the patent subsequent to May 10, 1967, has been disclaimed

U.S. Cl. 8—30 4 Claims

ABSTRACT OF THE DISCLOSURE

In the dyeing of hydrophobic fibers such as polyvinyl chloride fiber, polyacrylonitrile fiber, modified polyester fiber and cellulose acetate fiber with an anionic dyestuff, a method of further enhancing the dyeability of those of the said fibers which have in themselves a dyeing site for an anionic dyestuff and of making dyeable those of the said fibers which have hitherto had no dyeing site for an anionic dyestuff by the conjoint use of a compound of the following formula:

\[
\begin{array}{c}
R_1 \\
A, N - Z \\
R_2 \\
X
\end{array}
\]

Wherein \( R_1, R_2 \): lower alkyl or lower allyl, \( Z \): benzyl or naphthyl (may be substituted), \( A, R_1 \): butyl, or phenyl (may be substituted), \( X \): halogen or lower alkyl sulfonic acid residue.

This application is a continuation-in-part of application Ser. No. 609,309, filed Jan. 16, 1967, now abandoned.

The instant invention is directed to a method of dyeing polyvinyl chloride, polyacrylonitrile, modified polyester or cellulose acetate fibers with anionic dyestuffs. In particular, the instant invention is directed to a method of dyeing the above-noted fibers with anionic dyestuffs in the presence of at least one compound having the general formula:

\[
\begin{array}{c}
R_1 \\
A, N - Z \\
R_2 \\
X
\end{array}
\]

wherein \( R_1 \) and \( R_2 \) are groups selected from the class consisting of lower alkyl and lower allyl substituents having from about 1 to about 4 carbon atoms, \( Z \) is selected from the class consisting of benzyl and naphthyl substituents, \( A \) is selected from the class consisting of butyl and phenyl substituents, and \( X \) is selected from the group consisting of halogen atom and lower alkyl sulfonic acid residues.

Numerous techniques of dyeing polyvinyl chloride fiber are well known in the art. Exemplary of such techniques are dyeing methods which comprise preparing an insoluble complex with an acid dye and a cationic surface active agent and subsequently, dyeing with said complex. It is noted, however, that the previously known techniques have been unsatisfactory in providing dyes of relatively deep shades. Therefore, a primary object of the instant invention is to provide a dyeing method by which fibers may be fully dyed to a satisfactorily deep shade.

Yet another object of the instant invention is to provide a dyeing technique by which polyvinyl chloride fibers may be satisfactorily dyed to a deep shade.

A still further object of the instant invention is to provide a dyeing technique whereby numerous other textile materials may be satisfactorily dyed to a relatively deep shade.

Polyacrylonitrile fiber is normally dyed with cationic dyestuffs. However, when such cationic dyestuffs are employed and, further, when one desires to expand the colors which may be utilized, and, further, eliminate the difficulties in dyeing of mixed spun products. The use of an acid dye is generally considered preferable. Therefore, a still further object of the instant invention is to provide a dyeing process which easily facilitates the expansion of colors which may be dyed in connection with polyacrylonitrile fiber and mixed spun products.

A still further object of the instant invention is to provide a dyeing process which is particularly well suited for use in connection with mixed spun products in which one of the fibers is wool.

Polyester fiber has conventionally been dyed by the use of dispersed and/or azoic dyestuffs. However, such polyester fiber which has been so treated has not been found to be completely satisfactory inasmuch as the dyestuffs employed and the reaction of said dyestuff with the polyester fiber does not result in a dyed substrate having a desired degree of brightness. That is to say, that when such dispersed and/or azoic dyestuffs were employed the brightness of the dyes was inferior to that of an acetate fiber dyed with a dispersed dye, a nylon fiber dyed with acid dyes, and/or acrylic fiber dyed with a cationic dye.

Furthermore, such polyester fibers dyed with dispersed and azoic dyestuffs are also unsatisfactory in connection with its color fastness to sublimation. It is also known in the art to treat modified polyester fibers with acid dyes which is made possible by the introduction of active sites for the acid dyestuffs into the fiber material. Such techniques have, however, been unsuccessful to date. It is, therefore, a further object of the instant invention to provide a dyeing technique by which one can dye modified polyester fibers in bright shades and, further, which technique also provides a dyeing which has improved color fastness to sublimation.

Cellulose acetate fiber has also been dyed with dispersed dyestuffs in a manner similar to that employed with polyester fibers described above. It is noted, however, that there are numerous drawbacks associated with such dyes such as a lack of brightness in the dyed product and the like. Therefore, a further object of the instant invention is to provide a dyeing technique which is useful in connection with cellulose acetate fiber which technique may be utilized to provide extension bright shades and, further, to facilitate the dyeing of such fibers.

These and other objectives of the instant invention will become more evident from the following more detailed description thereof.

It has been found that the foregoing objects of the instant invention may be achieved by dyeing polyvinyl chloride, polyacrylonitrile, modified polyester and cellulose acetate fibers with an anionic dyestuff in the presence of at least one compound having the general formula:

\[
\begin{array}{c}
R_1 \\
A, N - Z \\
R_2 \\
X
\end{array}
\]

wherein \( R_1, R_2 \) are groups selected from the class consisting of lower alkyl group and lower allyl group, having 1-4 carbon atoms. \( Z \) is a group selected from the class consisting of benzyl group and naphthyl group, and \( X \) may have a substituent, \( A \) is a group selected from the class consisting of butyl group and phenyl group, said phenyl
3,700,399

3 group may have a substituent, and X is selected from the group consisting of halogen atom and lower alkyl sulfonic acid residue.

Techniques for depositing anionic dyes on hydrophobic fibers possessing substantially no sites for said dyes have been known heretofore. One such method comprises making a substantially water insoluble complex by conjoint use of a cationic surfactant with an anionic dye stuff such as acid dyes or direct dyes so as to effect the dye adsorption. Such techniques, however, have not been suitable to produce satisfactory dyeings especially when applied to polyvinyl chloride, polyacrylonitrile, modified polyester and cellulose acetate fibers, i.e., the fibers subject to the process of the instant invention, even though said fibers are similarly hydrophobic. It has therefore, quite unexpectedly been found that the above-noted fibers may be dyed by the process of the instant invention wherein an anionic dye stuff is employed in combination with the above-noted compounds so as to effect the dyeing of said fibers.

The process of the instant invention, as noted above, comprises the conjoint use of the compound represented by Formula I in combination with an anionic dye stuff. It has been found that by use of such compounds it is possible to dye fibers which have hitherto been undyeable and/or which have been scarcely dyable by anionic dye stuffs.

Although the details of the theory of the method of the present invention are not clear, it is believed that the water-soluble or water-dispersible dye forms a complex with the aforesaid compound to become less insoluble in water and at the same time before compatible with and have affinity for the hydrophobic fiber, with the consequence that this compound diffuses into the interior of the fiber owing to the elevated temperature and, at times, the action of the carrier to effect the adsorption of the dye. Hence, the balance between the size of the complex of the dye and the compound and its compatibility and affinity relative to the hydrophobic fiber becomes an important factor in determining the amount of dye adsorption. Thus, the intended results cannot be obtained only by making dyes water insoluble. The intended results can be only obtained when the specific compounds as prescribed by this invention are used. Experimental of the compounds represented by Formula I are the following:

butyldialkybenzyl ammonium salt
butyldialkynaphthyl ammonium salt
diallyldialkybenzyl ammonium salt
diallyldialknaphthyl ammonium salt
tributylbenzyl ammonium salt
tributynaphthyl ammonium salt
phenyldialkybenzyl ammonium salt
phenyldialknaphthyl ammonium salt
tolylalkylbenzyl ammonium salt
tolylalkynaphthyl ammonium salt

It is to be noted that the above compounds are merely representative of those encompassed by Formula I set forth above. In this connection, it is noted that said compounds may also contain a substituted phenyl, benzyl or naphthyl group wherein said grouping is substituted by an alkyl such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and the like, an alkoxo substituent such as methoxy, ethoxy, propoxy, butoxy and the like, a halogen substituent such as chlorine, bromine, iodine and the like or numerous other substituents.

When dyeing polyvinyl chloride fiber it is noted that preferably one employs a butyldialkybenzyl ammonium salt or a trialkynaphthyl ammonium salt. More specifically, the preferred salts for use in connection with polyvinyl chloride are the tri-n-butylbenzyl ammonium salt or the tributyl-2,3-dichlorobenzyl ammonium salt which have been found to provide superior results. When dyeing polyacylonitrile fiber, preferably one employs tributylbenzyl ammonium salt, tributynaphthyl ammonium salt, or a halosubstituted and, in particular, chlorine substituted benzyl or naphthyl derivative salt.

In connection with modified polyester fibers, it is noted that superior dyeings are obtained especially when one employs the preferred N-tributyl benzyl ammonium salt and/or the tributyl naphthyl ammonium salt. When cellulose acetate fibers are the subject of the dyeings, the use of tri-N-butylbenzyl ammonium salt, the phenyl dimethylbenzyl ammonium salts, the phenyl diethyl benzyl ammonium salt, or the tolyldimethylbenzyl ammonium salt is preferred. It is noted, that one may employ mixtures of the compounds represented by Formula I and further mixtures of the preferred compounds noted above in connection with each specific fiber.

It is noted that the polyvinyl chloride fibers suitable for use in connection with the instant invention may be homopolymers, copolymers or polyvinyl chloride fibers which have after chlorinated. That is to say, that any polyvinyl chloride is suitable for use in connection herewith.

It is also noted that the subject process may be applied either to the fiber individually and/or to mixed knitted or woven fabrics comprising polyvinyl chloride either alone or in combination with other fibers. It is noted that when the subject process is applied to a mixed spun product comprising polyvinyl chloride fiber in combination with another fiber which other fiber is preferably wool that one can advantageously dye both fibers simultaneously in one bath with the same acid dye.

In connection with the polyacrylonitrile fibers usable in the process of the instant invention, it is noted that a polyacrylonitrile which does not have a dyed site for an anionic dye is employed, which fibers are of course, well known in the art. It is also noted that the process of the instant invention may be employed in connection with mixed knitted or woven fabrics comprising the above-noted fibers in combination with other fibers.

The modified polyester fibers employed in connection with the instant invention are those so-called readily dyeable polyester fibers. That is to say, that said modified polyester fibers are those whose dyeability by means of dispersed dyes have been improved by heat treatment at elevated temperatures and/or by the introduction of a secondary component. The terminology "readily dyeable polyester fibers" as employed herein is defined to mean those in which the percentage exhaustion of the dye bath as determined in accordance with JIS L 1060-1960 is above 70%. Satisfactory dyeings cannot be obtained even by the method of the instant invention in those situations wherein the percentage exhaustion of the dye bath is below the above-noted level.

The measurement of dye absorption in connection with JIS L 1060-1960 is as follows:

The specimen is washed in a 100-fold amount of distilled water (70° C) for 30 minutes with stirring, followed by air drying and thorough opening of the fiber. One gram of the so standardized specimen is weighed and dyed under the following conditions:

dye stuff; Dispersol Fast Scarlet B 150 pf (C.I. Disperse Red 1)—4% O.W.F.
dispersing agent; Marseille soap—0.5 g./l.
goods to liquor ratio—1:100
temperature—boiling temperature
duration—90 minutes
stirring—once per 20 seconds

After completion of the dyeing and cooling to room temperature, a suitable amount of the remaining dye liquor is taken and combined with an equal amount of C.P. acetone (reagent); then this acetone-water (1:1) mixture is diluted 25 times and the optical density is measured using a spectrophotometer. Next, the dye liquor is diluted in a similar manner and is measured for its optical density. The rate of dye absorp-
tion is then obtained by the following equation, the average of three measurements rounded to whole numbers being used:

\[ \text{Dye absorption (percent)} = \left(1 - \frac{d_0}{d} \right) \times 100 \]

where \(d_0\) = optical density of the dye liquor before dyeing and \(d\) = optical density of the remaining liquor after dyeing.

The cellulose acetate fibers which may be employed in connection with the instant invention include diacetate or triacetate fibers. Furthermore, the instant invention is also applicable to so-called fiber-acetylated staples. As noted above, the process of the instant invention is also suitable for use in connection with mixed knit and/or woven knit or woven fabrics of the subject fibers in combination with other fibers. It is noted that the process of the instant invention is especially effective in the case of mixed fibers wherein a cellulose acetate fiber is mixed with a polyamide fiber in view of the fact that both the polyamide and the cellulose acetate are dyed with acid dyes.

The anionic dyestuffs suitable for use in connection with the instant invention are all dyestuffs which have an anionic group. Exemplary of such dyestuffs are the acid dyes, direct dyes, metal complex dyes, mordant dyes, water-soluble reactive dyes, metal complex dyes of the disperse type, and the like. Generally, the use of an acid dye brings about a maximum effect and it is preferred that such a dye have a small number of water soluble groups in its dye molecule. Normally, a dye having one to two water soluble groups gives an excellent effect.

In practice the instant invention may be employed by any of the conventional techniques such as dipping, padding or printing wherein the dyestuff is contacted with a textile in any form such as a staple yarn, fabric form, and the like. The conditions for dyeing are varied depending upon the class of textiles employed therefor, and, further the dyeing technique utilized. For example, one may employ the dyeing conditions utilized in connection with the most popular dipping method as follows: In the case of polyvinyl chloride fiber, a compound having Formula I was added to the dye bath in an amount of from about 1-100% O.W.F. (percentage by weight based upon the material to be dyed) and the dyeing is carried out at a temperature of from about 60 to about 100° C. In the event polyacrylonitrile fiber is to be dyed, about 1-100% O.W.F. of the aforesaid compound is added to the dye bath and the dyeing is carried out at a temperature above approximately 100° C. and preferably, at a temperature of from about 110 to about 130° C. until the intended depth of color phase is obtained. When cellulose acetate fiber is employed, from about 1-100% O.W.F. of the above-compound is added to the dye bath and dyeing is carried out at a temperature of from about 80 to about 130° C. It is noted that preferably the temperature is as high as possible so long as no adverse effects incurred thereby.

It is noted that the process of the instant invention may be further enhanced by employing conventional carriers as dyeing accelerating agents. Exemplary of such carriers are phenolic compounds such as o- and p-phenylphenol, the chlorobenzene compounds such as monochlorobenzene, o-dichlorobenzene, and trichlorobenzene, the benzoic acid compounds such as benzoic acid and salicylic acid, naphthalene compounds such as methyl naphthalene, and the like.

Of the above carriers, it is noted that those which are water-soluble may be added to the dye bath as an aqueous solution whereas those which are water-insoluble are added in the form of a dispersion or an emulsion.

A non-ionic surfactant is also preferably employed in connection with the process of the instant invention in an amount suitable therefor. The nonionic dyestuff is generally employed as a leveling agent so as to thoroughly disperse the dye and prevent said dye from turning tarry, thus, enhancing the ultimate dyeing. Such surfactants are those which are commonly employed as dispersing agents and include for example, polyethylene glycol, type surfactants such as polyethylene glycol alkylamine, polyethylene glycol alkyl ethers and polyethylene glycol aliphatic acid esters, and the ether or ester type surfactants having polyhydric alcohols as their hydrophilic group, such as sorbitan aliphatic acid esters and aliphatic acid monoglycerides.

The fibers which have been dyed according to the invention method are, after dyeing, subjected to thorough soaping and, if necessary, to reduction clearing, and the dyeing is fully colorfast after these post treatments. It is noted that one of the advantages of the subject dyeing process is that the conjoint use of an anionic dye-stuff and the cationic compound specified by Formula I, above, it has been found possible to dye the aforementioned fibers which have hitherto been undyeable or unsatisfactorily dyable.

Although the details of the theory of the invention method are not clear, it is believed that the water-soluble or water-dispersible dye forms a complex with the aforesaid compound to become less insoluble in water and at the same time becomes compatible with and have affinity for the hydrophobic fiber, with the consequence that this compound diffuses into the interior of the fiber owing to the elevated temperature and, at times, the action of the carrier to effect the adsorption of the dye. Hence, the balance between the size of the complex of the dye and the compound and its compatibility and affinity of the hydrophobic fiber becomes an important factor in determining the amount of dye adsorption. Thus, the intended results cannot be obtained only by making dyes water-insoluble. The intended results can be only obtained when the specific compounds prescribed by this invention are used.

The instant invention will now be illustrated by the following more detailed examples thereof. It is to be noted, however, that the instant invention is not deemed as being limited thereto.

**EXAMPLE 1**

**Summitil Fast Red B (C.I. Acid Red 6, C.I. No. 19690).... 2% O.W.F.**

![Chemical structure of Summitil Fast Red B](image)

**Condensation product of 1 mol of nonylphenol and 20 mols of ethylene oxide.**

**Methyl naphthalene (carrier).... 3 g. liter.**

**Glands to liquor ratio.**

**1:100.**

0.04 gram of the above-noted acid dye and 0.2 gram of the condensation product of nonylphenol and ethylene oxide were dissolved in 100 cc. of water and 0.4 gram of a carrier of emulsified methylhyphenylene added thereto. Subsequent to said addition, 0.1 gram of the above-noted cationic compound was added to the solution and the solution charged into a 500 cc. beaker which was controlled to have 200 cc. of total liquid amounts so as to provide a goods to liquor ratio of 1:100. 2 grams of spun fiber of polystyrene chloride fiber were dipped in the dye liquor at 40° C. and the temperature was gradually elevated for 30 minutes. The dyeing was conducted for 60 minutes at 100° C. The dye product obtained was subjected to washing thoroughly with water and soaping with a solution containing 1 gram of soap at 60° C. for 20
3,700,399 7 minutes. The dye product obtained exhibited a bright red shade and the adsorption ratio of dye was 85%.

EXAMPLE 2

When Example 1 was repeated except that a compound of the formula

was used instead of the cationic compound, used in said example, a product dyed a deep bright red shade was obtained.

EXAMPLE 3

A 1:1 type metal complex dyestuff Neolan Black WA (C.I. Acid Black 82, C.I. No. 15771) having the formula: Chromium complex derived from


was employed. The resultant product was found to have been dyed a red shade.

EXAMPLE 5

The procedure of Example 3 was repeated utilizing in lieu of the dyestuff therein a 1:2 type metal complex dyestuff Neolan Red B (C.I. Acid Red 201, C.I. No. 18761) having the structure:

was dissolved in 200 cc. of water together with 0.5 g. of a non-ionic surfactant (chief constituent; C_{12}H_{25}O(C_{6}H_{4})_{12}H)

serving as a dye dispersing agent. 1 g. (10%) of a cation compound of n-tributylbenzyl ammonium chloride and a carrier of emulsified α-methyl naphthalene were further added in this solution whereby a dye liquor was made. This dye liquor was charged in the dye bath of a high pressure dyeing apparatus and water was added to adjust a goods-to-liquor ratio 1:50. The total amount of the dye liquor was kept to 500 cc.

After dipping 10 g. of modified polyester fibers having 85% of the dye absorption ratio measured in accordance with the JIS in the dye liquor of above-described composition, the dye bath of the high pressure dipping apparatus was tightly closed and the temperature was gradually elevated at 130° C. for 40 minutes. The dyeing was conducted at 130° C. for 90 minutes and thereafter, the temperature was gradually lowered. The dyed product was then taken out and subjected to washing with water.

2.5 g. of a methyl naphthalene carrier and 0.5 g. of a potassium dichromate were dissolved in 500 cc. of water and a solution of chromic acid which was adjusted to maintain the pH 3 with sulfuric acid, was charged in the said dye bath of the dyeing apparatus. The said dyed product washed with water was dipped in this solution of chromic acid. The temperature was elevated to 100° C. and thereafter the chrome treatment was conducted for 40 minutes. After the completion of the chrome treatment, the temperature was gradually lowered and the dyed product (black) was taken out. In a solution of 1 g. each of a hydrosulfit

and a NaOH this black dyed product was dipped and subjected to reduction clearing at 80° C. for 30 minutes whereby the dye product was dyed a deep black shade.
EXAMPLE 7
Kayagyi Sky Blue R (C.I. Acid Blue 62, C.I. No. 62045) having the formula:  

\[
\begin{align*}
\text{O} & & \text{NH}  \\
\text{SO}_{\text{Na}} & & \\
\text{CH} - \text{CH}_2 & & \text{CH} - \text{CH}_2
\end{align*}
\]

n-Tributylbenzyl ammonium chloride.............................. 10% O.W.F.  
\[
\text{C}_9\text{H}_{13\text{a}} \text{NN-C N N ? p CE n-Tributyl-4-chlorobenzyl-annionium} \text{SO}_{\text{Na}} \text{Cr- NN-C N N ? p CE}
\]

Goods to liquor ratio............................................. 1:30.

A crepe de Chine fabric of diacetate fiber was dipped in a dyebath of the composition indicated above and dyed for 60 minutes at 80° C. After completion of the dyeing, the fabric was submitted to a soaping treatment in a bath containing an anionic surfactant, thereby obtaining a product dyed a bright deep blue shade.

EXAMPLE 8
The procedure of Example 7 was repeated with the exception that a triacetate fiber was used in lieu of a diacetate fiber. The dyeing was carried out at a temperature of 120° C, and the product dyed a deep blue shade was obtained.

EXAMPLE 9
Suminoil Fast Red of Example 1 (C.I. Acid Red 6, C.I. No. 14680)—3% O.W.F.  
Phenyldimethylbenzylammonium chloride—9% O.W.F.  
\[
\text{C}_9\text{H}_{13\text{a}} \text{O(CH}_2\text{H}_2\text{O)}_3\text{H}-2.5 \text{ O.W.F.}
\]

Goods to liquor ratio—1:50.

A plain weave of mixed filament yarns of nylon 6 and diacetate was dipped in a dye bath of the composition indicated above and dyed for 60 minutes at 100° C. After completion of the dyeing, the fabric was submitted to a soaping treatment in a bath containing an anionic surfactant, thereby obtaining a product dyed bright red having same shade.

EXAMPLE 10
A polycrystalline staple fiber was dyed for 60 minutes at 110° C. with the use of a dye bath of the composition indicated below, and a deep red dyeing was obtained.

Suminoil Fast Red of Example 1 (C.I. Acid Red 6, C.I. No. 14680)—2% O.W.F.  
Condensation product of 1 mol of laurylalcohol and 20 mols of ethylene oxide—3% O.W.F.  
n-Tributylbenzyl ammonium chloride—10% O.W.F.

Goods to liquor ratio—1:100.

EXAMPLE 11
A polycrylonitrile staple fiber was dyed for 60 minutes at 100° C. with the use of a dye bath of the composition indicated below, and a deep yellow dyeing was obtained.

Supramine Yellow R (C.I. Acid Yellow 26, C.I. No. 18855) having the formula:

\[
\begin{align*}
\text{N} & & \text{N}  \\
\text{CH}_2 & & \text{SO}_{\text{Na}}  \\
\text{N} & & \text{N}
\end{align*}
\]

n-Tributyl-4-chlorobenzyl-ammonium chloride........................ 10% O.W.F.  
Condensation product of 1 mol of laurylalcohol and 20 mols of ethylene oxide—3% O.W.F.

Goods to liquor ratio............................................. 1:30.

EXAMPLE 12
A crepe de Chine diacetate fabric was dipped in a bath having the following composition:

Kayagyi Sky Blue R of Example 20 (C.I. Acid Blue 62, C.I. No. 62045)  
D-butyln, methyl benzyl ammonium metho sulphate  

\[
\begin{align*}
\text{C}_9\text{H}_{13\text{a}} \text{N-C CH} & & \text{CH}_2 \\
\text{CH}_2 & & \text{CH}_2
\end{align*}
\]

Nonionic surfactant of the formula:

\[
\begin{align*}
\text{C}_9\text{H}_{13\text{a}} & & \text{O(CH}_2\text{H}_2\text{O)}_3\text{H}
\end{align*}
\]

Liquor ratio......................................................... 1:30.

Subsequently, the temperature was gradually elevated, and a bright deep blue shade was obtained by carrying out the dyeing for 90 minutes at 90° C. The color fastnesses, especially fastness to wetting, of the dyed product obtained were very excellent to a degree that they could not be effected by disperse dyes.

EXAMPLE 13
A crepe de Chine diacetate fabric was printed using a paste having the following composition:

<table>
<thead>
<tr>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kayagyi Sky Blue R (C.I. Acid Blue 62, C.I. No. 62045)........</td>
</tr>
<tr>
<td>Methyl, allyl benzyl ammonium metho sulphate..................</td>
</tr>
</tbody>
</table>
| \[
\begin{align*}
\text{C}_9\text{H}_{13\text{a}} \text{N-C CH} & & \text{CH}_2 \\
\text{CH}_2 & & \text{CH}_2
\end{align*}
\] |
| Thiodiethylene glycol........................................... | 2 |
| Thixotrope dispersing agent: bean gum.......................... | 70 |
| Water.................................................................. | 10 |

The printed fabric was dried, steamed for 40 minutes at 100° C, and then washed with water. A dyeing of a deep shade was obtained.

What is claimed is:

1. A method of dyeing a textile fiber selected from the group consisting of polyvinyl chloride fiber, polycrylonitrile fiber lacking a dye site for an anionic dye, modified, readily dyeable polyester fiber in which the percentage exhaustion of the dye as determined by JIS L 1060—1960 is above 70% and cellulose acetate fiber which comprises dyeing said fiber with an anionic dyestuff in the presence of at least one compound of the general formula

\[
\begin{align*}
\text{R}_1 & & \\
\text{R}_2 & & \text{X}
\end{align*}
\]

wherein R₁ and R₂ are selected from the group consisting of lower alkyl substituents and lower alkyl substituents having from 1 to 4 carbon atoms, Z is selected from the group consisting of benzyl, naphthyl, substituted benzyl, wherein the substituent is selected from alkyl of 1 to 4
carbon atoms, alkoxy of 1 to 4 carbon atoms, and halogen, and substituted naphthyl, wherein the substituent is selected from alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, and halogen, and \( X \) is selected from the group consisting of halogen atom and lower alkyl sulfonic acid residue.

2. A method of dyeing a textile fiber selected from the group consisting of polyvinyl chloride fiber, polyacrylonitrile fiber, modified, readily dyeable polyester fiber in which the percentage exhaustion of the dye as determined by JIS L 1060–1960 is above 70\% and cellulose acetate fiber, which comprises dyeing said fiber with an anionic dyestuff in the presence of at least one compound of the general formula:

\[
\begin{array}{c}
C_{\alpha}H_{\beta}\bigg[
\begin{array}{c}
C_{\gamma}H_{\delta}\bigg[
\begin{array}{c}
\text{N—Z}
\end{array}
\bigg]
\end{array}
\bigg]X^{\Theta}
\end{array}
\]

wherein \( Z \) is a group selected from benzyl, naphthyl; substituted benzyl, wherein the substituent is selected from alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, and halogen, and substituted naphthyl, wherein the substituent is selected from alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, and halogen; and \( X \) is selected from the group consisting of halogen atom and lower alkyl sulfonic acid residue.

3. The method according to claim 2 wherein the said compound is tri-n-butylbenzyl ammonium salt.

4. The method according to claim 2 wherein the said compound is tri-n-butylnaphthyl ammonium salt.

References Cited

UNITED STATES PATENTS

2,492,394 12/1949 Olpin et al. 8—56
2,094,082 9/1937 Rendell et al. 8—5
2,828,180 3/1958 Sertorio 8—62
2,676,987 4/1954 Lewis et al. 260—567.6
3,660,008 5/1972 Kissa 8—21 A

OTHER REFERENCES


GEORGE F. LESMES, Primary Examiner
P. C. IVES, Assistant Examiner

U.S. Cl. X.R.

8—21 B, 172, 162 B, 177 AB, 84; 260—567.6 M
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Delete the formula in Claim 2 and insert therefor:

\[
C_4H_9\xrightarrow{N}\text{Z}\xleftarrow{X}C_4H_9
\]

Signed and sealed this 10th day of April 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents