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METHOD OF DYEING NITROGENOUS
FIBERS WITH METALLIZED AZO
DYES

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This invention relates to the use of the reaction product of substituted triazines with low-molecular weight epoxides as dye assistants for metallized dyes in dyeing processes.

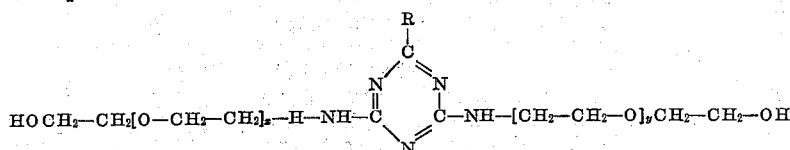
Fibers and fabrics, particularly basic nitrogenous materials such as wool, nylon, aralac, etc., have been dyed with metallized dyes by various processes, in one of which the dye is metallized in the form of a metal complex and then dyed onto the fiber from a bath. The compounds of this invention are advantageous for use in this process as well as other processes such as the metachrome process which involves simultaneously dyeing and metallizing, or the so-called top and bottom chrome process in which the dye and metal salts are applied separately.

It has been common practice to dye basic nitrogenous materials from a strongly acid dye bath with metallized dyes. A relatively strong acid bath has been necessary, and even with a large amount of acid the process has often resulted in dyeings which are not sufficiently level. The disadvantage of dyeing any fabric in a solution of a strong inorganic acid is obvious. Chemically, both wool and nylon are high-molecular-weight polyamides and in a boiling acid solution we have ideal conditions for the hydrolysis of the amide linkage. It is not surprising, therefore, that some hydrolysis does take place in the

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The difficulties involved in producing level shades have resulted from a number of factors, an important one being the inadequate or excessively slow penetration of the dye into the fiber. This poor penetration has led in the past to considerable experimentation. It was soon found that cationic surface active agents improved the penetration of metallized dyes in the fibers. This increased the strength of the dyeing, but it led to another serious difficulty, namely, scum formation. The metallized dyes contain acid groups and in the strong acid bath tend to react with cationic surface active agents to produce insoluble compounds forming a highly colored scum, which scum in many cases adhered locally to portions of the fabric and resulted in specky dyeing. Various procedures have been adopted to keep the scum in dispersed form so that the specks would not be too large. However, the palliatives used in the past have still left much to be desired.

We have now discovered a class of nonionic substituted triazines which, when used according to the process of this invention, result in a level dyeing but do not form objectionable scum in the dye bath. These compounds are polyalkylene oxide derivatives of 2-alkyl guanamines which, in the case of ethylene oxide derivatives, conform to the general formula



acid dye bath with the production of a lower molecular weight product that is reflected in decreased tensile strength and a harsh hand.

Although the dye chemist has recognized for years that strong, completely ionized acids should not be present in the dye bath, their use was continued because no other method was known that would produce as level dyeings. The dye bath was always a compromise between increasing the acid, the temperature and bath time to improve the dyeing, and decreasing the acid, the temperature and bath time to avoid excessive damage to the fabric. This has greatly restricted the field of utility of premetallized dyes, both of the completely metallized type and the so-called half-metallized complexes which contain less than the maximum amount of metal capable of entering into chemical combination in the complex.

in which R is an aliphatic hydrocarbon radical containing at least 7 carbon atoms and x plus y may vary between 9 and 98 depending upon the amount of alkylene oxide that is condensed. Although the above formula illustrates the product formed by the condensation of guanamine with ethylene oxide, it will be recognized that glycidol may be substituted for all or part of the ethylene oxide. Furthermore, various other alkylene oxides may be used, such as propylene oxide, isobutylene oxide and tetramethylene oxide.

It is possible to vary the ratio of alkylene oxide to substituted guanamine through a wide range, depending on the properties desired in the dyeing assistant. In general, we prefer to condense between about 40 and 75 moles of alkylene oxide with 1 mole of substituted guanamine. Inasmuch as the polyalkylene oxide chain is responsible for the water-solubility of the dye assistant,

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it will be recognized that the tendency to form scum will be reduced as the amount of alkylene oxide present in the molecule is increased. When the alkylene oxide condensed is ethylene oxide, and the ratio of ethylene oxide to substituted guanamine drops below 6 or 10 to 1, a condition is obtained where the dye assistant is so insoluble that objectionable scum interferes with its use.

The strength of the dyeing is an inverse function of the amount of alkylene oxide condensed with the substituted guanamine and therefore, the particular dye assistant which may be used to greatest advantage will be a compromise between obtaining satisfactory solubility and maximum strength of dyeing.

The hydrocarbon chain R as mentioned above, may be varied between 7 and 17 carbon atoms. We have found that when the aliphatic hydrocarbon constituent contains less than 7 carbon atoms, the resulting compound is no longer effective as a dyeing assistant.

In our Patent No. 2,470,080 which issued May 10, 1949 to American Cyanamid Company, we have described a particular type of nonionic surface active agent prepared by the reaction of an alkylene oxide with an alkanol amide of a thermally polymerized drying oil acid. These reagents were effective in producing better levelness in less time and markedly increased the color value when they were present in the dye bath. The substituted guanamine condensates of the present invention show some very important additional advantages over the dye assistants referred to above in that they are most efficient in the presence of an organic acid. It is now practical for the first time, to replace the sulfuric acid usually required in the dye bath by the much more weakly ionized organic acids. Thus a solution is offered to one problem which has plagued the dye industry ever since the first synthetic dye was obtained by Perkins. This substitution of a weaker organic acid for sulfuric acid will greatly reduce damage to the fiber. Tensile strength of the dyed fiber will be improved and a much softer hand is obtained.

It is an advantage of the dyeing assistants of the present invention that they may be used without the drawback of scum formation which had previously made the use of cationic surface active agents unsuitable as dyeing assistants. Effective amounts of the surface active agents of the present invention can be added to the dye bath without precipitation, even when the bath contains such salts as ammonium sulfate, sodium sulfate, and the like. These agents, in the quantities used, are stable in the presence of acid and permit the dye bath to be kept for a reasonable time without serious decomposition.

It is an advantage of the present invention that no problem is involved in regulating the concentration of these dye assistants, as they may be added to the dye bath in small portions to obtain maximum effectiveness with a minimum of precipitation and scum formation. This enables one to vary the concentration over a wide range. In addition, the dye assistants of this series may be tailor-made by regulating the amount of ethylene oxide present in the molecule to avoid scum formation in dye solutions of normal concentration.

We have found that these nonionic surface active dye assistants are particularly well adapted for the dyeing of loose yarns, such as carpet yarn, raw stock, slubbing and knitting yarns, and wool with a low twist in general.

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We have found that the substituted guanamines of the present invention reduce the time required for dyeing by as much as one-half, which decreased bath time represents a considerable economic saving. As we have pointed out above, it has long been recognized that dyeing in acid solutions at the boiling point is detrimental to the fabric and that the damage is related to the time during which the fabric is subjected to these conditions. An even greater advantage of the decreased bath time, therefore, is the resulting improvement in the physical properties of the dyed fabric.

The following specific examples will further illustrate the manner in which the present invention may be practiced. Parts are by weight.

Example 1

Stearoguanamine was prepared by the method described in Example 2 of U. S. Patent No. 2,309,679 and then condensed with the following quantities of ethylene oxide:

- A—11 moles ethylene oxide
- B—25 moles ethylene oxide
- C—35 moles ethylene oxide
- D—50 moles ethylene oxide
- E—100 moles ethylene oxide

It should be noted that the amount of stearoguanamine is 1 mole in each case. The reaction between the ethylene oxide and stearoguanamine proceeded smoothly at 110°–220° C.

Example 2

A dye bath was prepared using 250 cc. water, 0.1 g. of the chromium complex of the azo dye obtained by coupling diazotized 1-amino-2-hydroxy naphthalene-4-sulfonic acid to beta-naphthol, 0.4 g. of formic acid and 0.1 g. of the surface active agent prepared as Example 1A. Five grams of wool, pre-wet with water, were then introduced into the dye bath at about 120° F., the bath slowly raised to the boil with intermittent turning of the wool, and dyed for about 1½ hours at the boil. The water that evaporated during the boiling was replenished frequently in order to keep the liquor-wool ratio practically constant. When the dyeing was completed, the wool was removed, rinsed and air-dried. A second dyeing was prepared in the same manner, except the product of Example 1A was not added to the dye bath. This was used as a control dyeing.

The shade of the wool dyed in the bath in which the surface active agent was present was more level and much stronger than that of the wool dyed in the control bath.

Example 3

Example 2 was repeated except that the time of dyeing was limited to forty-five minutes. The shade of the wool dyed in the presence of the surface active agent was more level and stronger than that of the wool dyed in the control bath for 1½ hours.

Example 4

The general procedure of Example 2 was repeated, except 0.5 g. of formic acid was used instead of 0.4 g. formic acid. The result was generally similar to that obtained in Example 2.

Example 5

The procedure of Example 2 was repeated, using again 0.5 g. of formic acid and substituting for the dye of Example 2 the chromium com-

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plex of the azo dye obtained by coupling diazotized 1-amino-2-hydroxy-naphthalene-4-sulfonic acid to 1-hydroxy-naphthalene-8-sulfonic acid. Again the color value of the dyeing obtained from the bath in which the surface active material was present was much stronger and the shade was more level than the dyeing obtained in the control bath.

Example 6

The procedure of Example 2 was repeated, increasing the amount of formic acid to 0.5 g. and substituting the chromium complex of the azo dye obtained by coupling diazotized 1-amino-2-hydroxy-naphthalene-4-sulfonic acid to 1-phenol-3-methyl-5-pyrazoline. When the color value of the dyeing was determined by means of a spectrophotometer and compared against the control dyeing (an assigned value of 100%) the color value of the dyeing made in the presence of the surface active material was about 155%.

Example 7

The procedure of Example 2 was repeated, using 0.5 g. of formic acid and the chromium complex of the azo dye obtained by coupling diazotized 2-amino-4-chlor-phenol-6-sulfonic acid to 1-phenyl-3-methyl-5-pyrazolone. When the color value of the dyeing was determined by means of a spectrophotometer and the control sample was assigned a value of 100%, the color value of the sample dyed in the presence of the product of Example 1A was 165%.

Example 8

A dye bath was prepared using 250 cc. of water, 0.1 g. of the chromium complex of the azo dye obtained by coupling diazotized 4-nitro-2-amino-phenol to 1-(4'-sulfo-phenyl)-3-methyl-5-pyrazolone, 0.4 g. of formic acid and 0.1 g. of the surface active agent prepared in Example 1A. The color value of the dyeing obtained from the bath in which the surface active material was present was much stronger and the shade was much more level than that of the dyeing made in the control bath.

Example 9

The procedure of Example 8 was repeated, except that 0.1 g. of the surface active material described in Example 1B was used instead of the dye assistant of Example 1A. The dyeing made in the bath in which the surface active material was present was substantially equal to that in Example 8 and notably superior to that made in the control bath.

Example 10

The procedure of Example 8 was repeated, except 0.1 g. of the product described in Example 1C was used. The dyeing obtained in the bath containing the surface active material was slightly more level and somewhat weaker than the dyeing obtained in Example 8 which employed the surface active agent of Example 1A. Both dyeings, however, were markedly superior to the control dyeing.

Example 11

The procedure of Example 8 was repeated, substituting 0.1 g. of the product described in Example 1D. The results were very similar to those obtained in Example 9.

Example 12

The procedure of Example 8 was repeated, sub-

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stituting the surface active agent described in Example 1E. The wool dyed in the bath containing this product was notably stronger and much more level than the control dyeing. It was also more level than the dyeing obtained in Example 8. However, the shade was somewhat weaker than that obtained in Example 8.

This series of examples from 8 to 12 illustrates the principle mentioned above, namely, that increasing the amount of ethylene oxide improves the levelness of the dyeing and decreases the color value.

Example 13

The procedure of Example 2 was repeated, substituting 0.1 g. of the product of Example 1C for the product of Example 1A. The dyeing made in the bath in which the surface active material was present was much stronger and more level than the dyeing made in the control bath.

Example 14

The procedure of Example 2 was repeated, substituting the dye assistant of Example 1C and decreasing the amount to 0.025 part ($\frac{1}{4}$). The wool dyed in this bath was slightly weaker in color than that of Example 13, but was stronger than the wool dyed in the control bath.

Example 15

The procedure of Example 2 was repeated, using 0.15 g. of the surface active agent described in Example 1C. Wool dyed in the bath containing 0.15 g. of dye assistant was stronger and more level than wool dyed in the control bath.

Example 16

The procedure of Example 2 was repeated, using 0.5 g. of the product described in Example 1C in the dye bath. Wool dyed in this bath was very much stronger and more level than wool which was dyed in the control bath in the absence of any dye assistant.

Example 17

A dye composition was prepared consisting of 29 parts of the chromium complex of the azo dye obtained by coupling diazotized 1-amino-2-hydroxy-naphthalene-4-sulfonic acid to 1-hydroxy-naphthalene-8-sulfonic acid, 35 parts of the chromium complex of the azo dye obtained by coupling diazotized 1-amino-2-hydroxy-naphthalene-4-sulfonic acid to beta naphthol, 17 parts of the chromium complex of the azo dye obtained by coupling diazotized 1-amino-2-hydroxy-naphthalene-4-sulfonic acid to 1-phenol-3-methyl-5-pyrazolone, and 19 parts of Glauber's salt. A dye bath was prepared, using 250 cc. water, 0.1 g. of the dye mix described above, 0.5 g. of formic acid and 0.1 g. of the product of Example 1A. A control dyeing was also made in the absence of any surface active material.

The color value of the dyeing as made in the two baths was then determined by means of the spectrophotometer and the dyeing made in the presence of the dye assistant had a value of about 250% based on 100% for the control sample.

Example 18

α -Ethylhexanoguanamine was prepared according to the method described in Example 11 of U. S. Patent No. 2,309,679 and then condensed with 25 mol equivalents of glycidol to give a product that was readily soluble in water. This dye assistant was then used according to the

method of Example 2 to effect a strong and level dyeing on wool.

Example 19

By a reaction similar to that described in Example 1, lauroguanamine was prepared and condensed with 30 moles of glycidol by heating with stirring, to 130° C., whereupon an exothermic reaction took place, continuing for about 15 minutes. During this interval, the temperature of the reaction was maintained at 132-137° C. by cooling the reaction vessel in a water bath. The product was a pale yellow, transparent, viscous resin which was readily soluble in water. This surface active agent was used according to the method of Example 2 to improve the strength and levelness of wool dyeing.

Example 20

A dye bath was prepared with 300 cc. of water and 0.4 g. of the cobalt complex of the azo-dye obtained by coupling 4-nitro-2-amino-phenol to 1-(4'-sulfo-phenyl)-3-methyl-5-pyrazolone. To this bath was added 0.5 g. of calcined Glauber's salt, 0.1 cc. of 56% acetic acid and 5 g. of thoroughly wet-out wool yarn. 10 cc. of a 1% solution of the product of Example 1 was introduced and the temperature raised to 180° F., whereupon 0.075 g. of formic acid was added. The dyeing was continued at the boiling point until a satisfactory shade had been obtained.

Example 21

A dyeing was made as in Example 2, except the copper complex of the dye obtained by diazotizing ortho-phenetidine and coupling with Schaefer's salt is substituted for the chromium complex of Example 2. A rust-colored shade having excellent color value was obtained.

Example 22

By a reaction similar to that described in Example 1, stearoguanamine was prepared and condensed with 40 mols of propylene oxide.

To a dye bath containing 0.1 part of the propylene oxide condensation prepared above, 4 parts of 10% hydroxy acetic acid and 1 part of the chromium complex of the azo-dyestuff from diazotized anthranolic acid and 1-(4'-sulfo-phenyl)-3-methyl-5-pyrazolone in 300 parts of water were added 5 parts of wool yarn which had been thoroughly wet out. The bath was brought slowly to the boil and maintained at the boil for sufficient time to complete the dyeing.

Yarn which was dyed in a control experiment without the advantage of this dye assistant was not level.

Example 23

Example 2 was repeated substituting 5 g. of nylon for the wool.

Nylon dyed in a control bath was much weaker

in shade than that dyed in the presence of the dye assistant.

It will be noted in all the above examples that the metallized dyes employed are the so-called "soluble" dyes which in an acid dye bath behave in all practical aspects as a true solution. It will be recognized that some of the larger dye molecules may be present in the colloidal state, but in the following claims we refer to these dyes which form stable dispersions in an acid dye bath, as "soluble metallized dyes."

We claim:

1. A method of dyeing nitrogenous fibers with metallized azo dyes soluble in acid baths, which comprises subjecting the material to be dyed to a dye bath containing metallized dye; formic acid; and an amount sufficient to be effective but insufficient to cause scum formation and excessive precipitation in the bath, of a 2-alkyl-guanamine; said alkyl group being an aliphatic hydrocarbon chain of 7 to 17 carbon atoms and said 2-alkyl guanamine having polyalkylene oxide chains attached to the amino nitrogens, said polyalkylene oxide chains containing at least 11 but not more than 100 ether oxygen atoms separated by at least 2 but not more than 3 carbon atoms; and said dye bath being further characterized by the absence of mineral acids.

2. The method of claim 1 in which the material to be dyed is wool.

3. The method of claim 2 in which the 2-alkyl guanamine is alpha-ethylhexano guanamine.

4. The method of claim 3 in which said polyalkylene oxide chain is a polyethylene oxide chain.

5. The method of claim 1 in which the 2-alkyl guanamine is stearoguanamine.

6. The method of claim 5 in which the material to be dyed is wool.

7. The method according to claim 1 in which said 2-alkyl guanamine is lauroguanamine.

8. The method of claim 7 in which said polyalkylene oxide chains are polyglycidol chains.

9. The method of claim 1 in which said polyalkylene oxide chains contain between 40 and 75 ethylene oxide units.

10. The method according to claim 9 in which the material to be dyed is wool.

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