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2,723,178

METHOD OF CONTROLLING THE MIGRATION OF METALLIZED DYES BETWEEN DYE BATH AND FABRIC

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This invention relates to the use of quaternary ammonium compounds as migratory agents for metallized dyes in dyeing processes.

Fibers and fabrics, particularly basic nitrogenous materials such as wool, silk, 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 in 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.

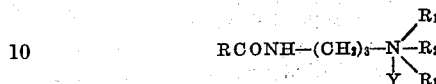
It has been common practice to dye basic nitrogenous materials such as wool, from a strongly acid dye bath with metallized dyes. A relatively strong acid bath has been necessary, and even with a large amount of acid the process has often resulted in dyeings which are not sufficiently level. The disadvantage 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 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 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.

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.

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We have now discovered a class of quaternary ammonium compounds which when used according to the process of this invention, do not form objectionable scum in the dye bath. These compounds are of the quaternary ammonium type which conform to the general formula



in which R is an aliphatic hydrocarbon radical containing at least 7 carbon atoms, R₁ and R₂ represent alkyl groups of low molecular weight, such for example, as methyl, ethyl, propyl, isopropyl, butyl, etc., R₃ represents a member of the group consisting of alkyl, hydroxy alkyl, aralkyl and unsaturated aliphatic hydrocarbon radicals, and Y represents an anion, such for example, as a halide, hydrogen sulfate, methyl or ethyl sulfate, alkyl phosphate, thiocyanate, etc. It will be recognized that the anion does not contribute to the specific property which is responsible for the effectiveness of this class of compounds and that the anion may be any ion which does not adversely affect the dye used.

In our prior 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 alkylol amide of a thermally polymerized drying oil acid. Those reagents were effective in producing better levelness in less time and markedly increased color value, even though they were in no sense cationic surface active agents. The quaternary ammonium salts of the present invention show some very important advantages over the nonionic dye assistants referred to above. It is now possible, 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 reduces or in many cases eliminates entirely, damage to the fiber. Tensile strength of the dyed fiber will be improved and a much softer hand is obtained.

The advantages of the present invention are obtained without the drawback of scum formation which had previously made the use of cationic surface active agents unsuitable as dye 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.

The migratory agents described herein provide the dyer with the best known method of product control. It frequently happens in present-day dyeing processes that, in the presence of inorganic acids, the desired shade will be exceeded, i. e., too strong a color developed. To compensate for this error when it occurs, it has been standard practice to reduce the shade by adding additional sulfuric acid to the dye bath, which treatment further decreases the useful life of the fabric. We have now discovered that a shade may be pulled down or built up by varying the concentration of the migratory agent. Thus if certain portions of the fabric become over-dyed and more strongly colored than other portions, the salts described herein will cause the dye to migrate to the

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fibers that are color deficient and leveling is obtained. If it becomes desirable, for any reason, to strip some of the dye from the fiber, this may be accomplished by increasing the concentration of the migratory agent. We are familiar with no other agent which will permit this precise control of the dyed product.

It is an advantage of the present invention that no problem is involved in regulating the concentration of the migratory agents as they may be added to the dye bath at any time. Unlike most dye assistants which must be added to the dye bath when it is first made up, the quaternary ammonium salts defined below may be added 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 the dye-stripping operation referred to above, the amount of quaternary ammonium salt may be increased up to the point where objectionable scum begins to form.

We have found that these cationic migratory agents are particularly well adapted for the dyeing of tightly twisted fabrics, such as gabardine, and the tightly twisted yarns, i. e., carpet yarn, where penetration is difficult. They are very effective in dyeing nylon-wool unions which have a tendency to produce a two-tone effect because of the difference in the physical and chemical structure of nylon and wool fibers.

Another application of this particular class of cationic surface active agents is for use as a scouring agent in an acid dye bath. In the processing of wool, the wool is first treated to remove as much of the bur or vegetable matter as possible, after which it is washed in an alkaline soap scouring train to remove the suint, oil, grease and organic materials. If this scouring job is properly done, so little grease remains in the wool that it cannot be worked physically in the yarn stage and on the loom without additional lubricant being added. For this reason, emulsifiable oils such as olive oil or specially prepared mineral and vegetable oils, are commonly added. These oils must then be removed prior to dyeing and unless they are rather completely removed, they are likely to interfere with the subsequent dyeing and produce uneven, splotchy results.

The addition of a cationic migratory agent such as stearamido propyl dimethyl hydroxy ethyl ammonium chloride to a dye bath makes it possible to scour out this mineral oil and do the dyeing in the same bath without any change in the dyeing process, thus eliminating one of the difficult operations and frequently a drying step in the processing of wool. It is thus possible to pass the yarns from the spinning frames directly into the dye bath and remove the oil in the conventional dyeing operation.

In addition to permitting dyeing to occur in the presence of these oils, it appears that the agent holds some of the oils in suspension and permits them to be absorbed and retained by the wool, resulting in a superior handle. Unexpectedly, this retention of some of the oil by fibers appears to have no effect whatever on the dyeing, so that it is possible to get both a better levelness and satisfactory dye bath exhaustion.

We have found that these quaternary ammonium compounds will reduce the time required for dyeing by as much as one-third. This 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.

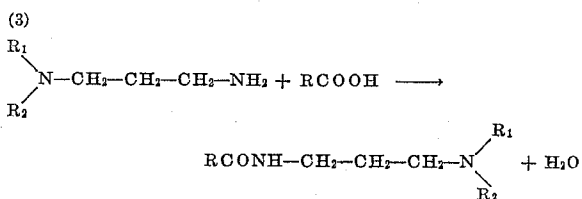
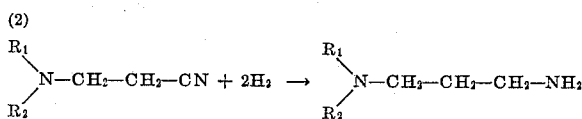
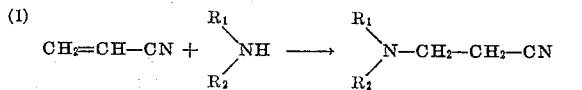
The following examples will further illustrate the manner in which the present invention may be practiced. Parts are by weight.

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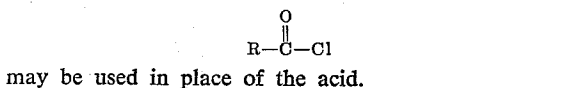
EXAMPLE 1

Preparation of stearamido propyl dimethyl hydroxy ethyl ammonium chloride

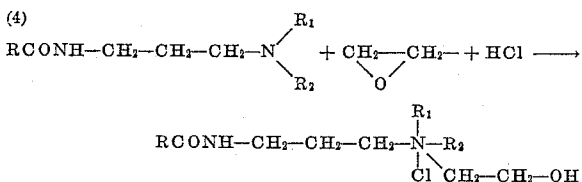
The reactions that are involved in the preparation of the quaternary ammonium salts may be outlined as follows:



As an alternative method for step (3), the acid chloride,



may be used in place of the acid.



Equimolecular quantities of dimethyl amine and acrylonitrile were mixed in a reaction vessel surrounded by water at 50° C. The reaction was carried out at approximately 50 pounds pressure to prevent volatilization of the low-boiling dimethyl amine. The product, beta-dimethyl amine propionitrile, was recovered by distillation at 90° C. at 50 millimeters pressure.

The nitrile was then reduced to the corresponding amine. In a typical reaction, 207 parts of beta-dimethyl amino propionitrile were hydrogenated in an autoclave under a pressure of about 90 atmospheres at 100° C. in the presence of 72.4 parts of anhydrous ammonia and about 8 parts of Raney nickel catalyst. The product was dried over solid potassium hydroxide and distilled at atmospheric pressure. The product, pure gamma-dimethyl amino propyl amine, has a boiling point of 132° C. at 760 mm.

The amine was reacted with an equimolecular quantity of stearic acid and the water of condensation was removed azeotropically by heating the reactants in the presence of boiling benzene until the distillate was clear. After removal of benzene, the gamma-stearamido propyl dimethyl amine was recovered as a tan liquid that solidified on standing.

To this tertiary amine was added about 150 parts of isopropanol based on the weight of the stearic acid amide and the pH of the solution was adjusted to approximately 4.0 with concentrated hydrochloric acid. This solution was then heated to 40 to 45° C. in a closed vessel and ethylene oxide introduced under about 15 pounds per square inch pressure. The ethylene oxide addition was continued until an equimolecular quantity had been absorbed, after which the isopropanol and unreacted ethylene oxide were stripped off by heating under reduced pressure. The product, gamma-stearamido propyl dimethyl hydroxy ethyl ammonium chloride, is a tan solid that is readily soluble in water.

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EXAMPLE 2

A dye bath was prepared from 300 parts of water and 0.1 part of the chromium complex of the azo dyestuff from diazotized anthranilic acid and 1-(4'-sulfo-phenyl)-3-methyl-5-pyrazolone. Two (2) parts of 10% sulfuric acid were added and five parts of wool yarn which had been thoroughly wet out was then introduced into the bath. 5.0 parts of a 1% solution of the product of Example 1 were then added and the bath brought slowly to the boil and maintained at the boil for sufficient time to complete the dyeing. The yarn was then removed, well rinsed, and dried. The dyeing was bright, level and of excellent color value.

A control dyeing was prepared as in the preceding paragraph except the surface active agent was omitted. The dyeing prepared in the control bath was definitely inferior in brightness, levelness and strength of shade to that prepared in the bath containing the surface active agent.

EXAMPLE 3

A dye bath was made up of 300 cc. of water and 0.1 g. of the chromium complex of the azo dyestuff obtained from coupling diazotized 4-nitro-2-amino-phenyl to 1-(4'-sulfo-phenyl)-3-methyl-5-pyrazolone. Three cc. of 10% ammonium sulfate solution were then added with four g. of calcined Glauber's salt. Thereupon 7.5 cc. of a 1% solution of the product of Example 1 were added and five g. of thoroughly wet out wool yarn were dyed in this bath. The bath was brought to the boil, boiled for about 30 minutes, 0.5 cc. of 56% acetic acid added, and the boiling continued for another 30 minutes, followed by an addition of 0.1 cc. of 56% acetic acid and the boiling then continued approximately 30 minutes, or until the dyeing was complete. The yarn was removed, rinsed and dried, and presented a bright dyeing which was level and had excellent color value.

A control dyeing was prepared as in the preceding paragraph except no surface active agent was added. The resulting dyed wool was quite inferior in brightness, levelness and strength of shade.

EXAMPLE 4

A dye bath was prepared as in Example 2 except the chromium complex of the azo dyestuff obtained by coupling diazotized 4-nitro-2-amino-phenol to 1-(4'-sulfo-phenyl)-3-methyl-5-pyrazolone was used. Wool dyed in this bath gave a very bright orange shade which was level and had excellent color value, whereas wool dyed in a control bath in which none of the surface active agent was present was much inferior in brightness, in levelness, and strength of shade.

EXAMPLE 5

The procedure of Example 2 was repeated except four parts of 10% formic acid were used instead of the two parts of 10% sulfuric acid. The dyeing obtained from the bath in which the surface active agent was present was stronger, brighter and more level than the dyeing obtained from the bath in which no surface active agent was present (control bath).

EXAMPLE 6

The procedure of Example 2 was repeated except 4 parts 10% hydroxy acetic acid were used instead of 2 parts of 10% sulfuric acid. The dyeing obtained from the bath in which the surface active agent was present was stronger, brighter, and more level than the dyeing obtained from the control bath.

EXAMPLE 7

The procedure of Example 2 was repeated except the surface active agent was not added until the dye bath had boiled for about 15 minutes. A good level dyeing was obtained which, however, was slightly inferior to that ob-

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tained when the surface active agent was added at the beginning of the dyeing.

EXAMPLE 8

The procedure of Example 2 was repeated except 10 parts of a 1% solution of the surface active agent instead of 5 parts as used in Example 2, were used in this example. While the dyeing was satisfactory, the color value was slightly inferior to that obtained in Example 2. This shows that the strength of the dyeing can be decreased slightly without impairing the levelness by altering the amount of the surface active agent added to the dye bath.

EXAMPLE 9

The procedure of Example 2 was repeated except the chromium complex of the azo dye obtained by coupling diazotized 1-amino-2-naphthol-4-sulfonic acid on 2-ethoxy-benzoyl acetonitrile was used. The dyeing obtained from the bath in which the surface active agent was present was stronger, brighter, and more level than the dyeing obtained from the bath in which no surface active agent was used.

EXAMPLE 10

The procedure of Example 2 was repeated except the chromium complex of the azo dyestuff obtained from diazotized 5-nitro-2-amino-phenol coupled to 2-amino-naphthalene-5,7-disulfonic acid was used. The dyeing obtained from the bath in which the surface active agent was present was stronger, brighter, and more level than the dyeing obtained from the control bath.

EXAMPLE 11

The dye bath was prepared with 300 parts of water and 0.4 part 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. 0.5 part of calcined Glauber's salt and 0.1 part of 56% acetic acid were then added, and 5 parts of thoroughly wet out wool yarn were introduced to the dye bath. 10 parts of a 1% solution of the product of Example 1 were introduced and the temperature raised to 180° F., whereupon 0.075 part of formic acid was added, the temperature raised to the boil, the bath boiled for a short time, 0.1 part sulfuric acid added and the boil continued for about an hour or until the dyeing was complete. A level orange shade was obtained.

EXAMPLE 12

A dye bath was prepared from 300 parts of water and 0.1 part of the chromium complex of the azo dyestuff obtained by coupling diazotized 1-amino-2-naphthol-4-sulfonic acid on 2-ethoxy-benzoyl acetonitrile. Two parts of 10% sulfuric acid were added and five parts of nylon yarn which had been thoroughly wet out were then introduced into the bath. Five parts of a 1% solution of the product of Example 1 were then added and the bath brought slowly to the boil and maintained at the boiling point for sufficient time to complete the dyeing. The nylon yarn was then removed, rinsed and dried. A level dyeing of improved color value as compared to the control dyeing was obtained.

EXAMPLE 13

The procedure of Example 10 was repeated except nylon was used instead of wool. A good level blue dyeing was obtained which was superior to the control dyeing.

EXAMPLE 14

A dye bath was made up of 300 cc. of water and the titanium complex of alpha diazo R-salt coupled to 4-sulfo naphthalene-1,8-sultone. 4 g. of 10% ammonium sulfate solution were then added with 5 g. of calcined Glauber's salt. 7.5 cc. of a 1% solution of the surface active agent of Example 1 were then added and 5 g. of thoroughly wet out wool yarn were introduced into the dye bath. This bath was heated slowly to the boil, boiled for about 45

minutes, after which 0.75 cc. of 56% acetic acid was added and the boiling continued for another 30 minutes. The yarn was then removed, rinsed and dried and a strong dyeing having a purple shade and good levelness obtained. A similar dyeing made in a control bath in which no surface active agent was present was much weaker and skittery.

EXAMPLE 15

The procedure of the preceding example was repeated except the dye was the cobalt complex of ortho-amino-phenyl-para-sulfonic acid on Schaeffer's salt. A very strong, excellent dyeing having a red shade was obtained in the bath in which the surface active agent was present, but in the control bath, only a very weak shade was obtained.

EXAMPLE 16

The procedure of the preceding experiment was repeated except the zirconium complex of the dye obtained by coupling alpha-diazo R-salt to 4-sulfo-naphthalene-1,8-sultone is used. Wool dyed in the bath containing the surface active agent was colored a good, rich purple while wool dyed in the bath in which no surface active agent was present was only slightly stained.

EXAMPLE 17

The procedure of Example 16 was repeated except the dye was metallized with nickel instead of cobalt. A strong, rich, red shade was obtained.

EXAMPLE 18

The copper complex of the dye obtained by diazotizing ortho-phenetidine and coupling with Schaeffer's salt was dyed on wool by the procedure of Example 2. A rust-colored shade having excellent color value was obtained.

EXAMPLE 19

A dye bath was prepared from 300 parts of water and 0.1 part of the chromium complex of the azo dye obtained by coupling diazotized 1-amino-2-naphthyl sulfonic acid on 2-ethoxy-benzoyl acetonitrile. 1½ parts of 10% sulfuric acid were added and two skeins of wool yarn which had been thoroughly wet were then introduced into the bath. After dyeing at the boiling point for 1 hour with an occasional addition of water to keep the volume approximately constant, the dyed skeins were removed, rinsed and dried. They were definitely skittery in appearance, and would have been unsatisfactory for commercial purposes.

One of these skeins was immersed in a solution containing 1½ parts of 10% solution of sulfuric acid and 2½ parts of 1% solution of the dye assistant of Example 1. After remaining in the solution at the boiling point for 45 minutes, the skein so treated was free of the skittery appearance, had a good color value and was bright and level.

In a control experiment the second skein of yarn was immersed in a solution of sulfuric acid containing 1½ parts of 10% sulfuric acid in 300 parts of water. After remaining in the acid solution at the boiling point for 45 minutes, the yarn had not lost its skittery appearance and was not as strong nor as bright as the wool which had been treated with the acid solution containing the migratory agent of Example 1.

EXAMPLE 20

The procedure of the preceding example was repeated except the dye of Example 10 was used. Again the skein dyed in the absence of the surface active agent retained its skittery effect even after the second acid treatment, whereas the skein which was removed from the original dye bath, rinsed, and dried, and then subsequently immersed in the bath containing the surface active agent became level, had excellent color value, good brightness, and was commercially acceptable. This indicates

that the dye was stripped from the wool and re-deposited in a level manner.

EXAMPLE 21

The procedure of Example 2 was repeated using, however, 10 parts of a 1% solution of the product of Example 1 and 5 parts of wool yarn containing 3-5% of a wool lubricating oil based on the weight of the wool. The resultant dyeing was level and bright and contained only 0.37% of the lubricating oil based on the weight of the wool. This dyeing was commercially satisfactory.

A control sample which was dyed without the addition of the product of Example 1 was uneven, dull, and contained 3.3% of the lubricating oil. This dyeing was not commercially acceptable. Furthermore, the wool had a greasy feel.

This example shows that the presence of the surface active agent causes the oil to be removed even in a dye bath, so that removal of the oil and dyeing can be obtained simultaneously. A value of 0.37% lubricating oil is not objectionable in a finished product.

EXAMPLE 22

Thirty-eight (38) parts of myristyl chloride were added drop-wise to a solution of 15.5 parts of N,N-dimethyl-propylenediamine in 160 parts of benzene. After one hour of stirring, the benzene solution was washed with 10% aqueous sodium hydroxide. The benzene layer was then washed once with water and the solvent removed by vacuum distillation. The residue was distilled at 208-215° C./1-2 mm., giving a solid distillate of γ -myristamidopropyl dimethylamine.

Two hundred sixty-six (266) parts of this amine was dissolved in 500 parts of cold alcohol and added to a solution of 46.8 parts of methyl chloride in 400 parts of alcohol in an autoclave at 0° C. The temperature was allowed to reach 85° C. and after the reaction had been completed, the myristamidopropyl trimethyl ammonium chloride was recovered by stripping off the alcohol under reduced pressure on a steam bath.

This product, when used according to the method of Example 2, gave markedly improved results over the control dyeing.

EXAMPLE 23

The preparation of gamma-palmitamido propyl trimethyl amine ammonium chloride

A mixture consisting of 200 parts absolute alcohol, 249 parts of gamma-palmitamido propyl dimethyl amine and 40.2 parts of methyl chloride dissolved in 250 parts of cold absolute alcohol were reacted in an autoclave at a temperature of 90° C. The product was recovered by stripping the alcohol under reduced pressure at 100° C.

This reagent, when used according to the method of Example 3, gave notably improved results over the control dyeing.

EXAMPLE 24

The preparation of stearamido propyl trimethyl ammonium chloride

Three hundred eighty (380) parts of stearamido propyl dimethyl amine and 200 parts of absolute alcohol were added to a cold solution of 56.8 parts methyl chloride and 300 parts of absolute alcohol in an autoclave. The reaction mixture was heated to 85° C. and stirred until the reaction was complete. The solvent was removed under reduced pressure at 100° C.

This product, when used according to the method of Example 11, produced a level orange shade on wool.

EXAMPLE 25

A mixture of 354 parts of lauramido propyl dimethyl amine and 65 parts of methyl chloride dissolved in alcohol were heated to 200° C. in an autoclave until the reaction was complete. The lauramido propyl trimethyl ammonium chloride was recovered by driving off the

alcohol at 100° C. under reduced pressure. The last traces of the alcohol were removed in a vacuum oven because of the foaming tendency.

This product was substituted for the dye assistant of Example 14 to give a strong purple shade of good levelness.

EXAMPLE 26

The preparation of abietamido propyl dimethyl hydroxyethyl ammonium chloride was accomplished by the method outlined in Example 1 above. A dye bath was prepared from 300 parts of water and .1 part of the chromium complex of the azo dyestuff of diazotized anthranilic acid and 1-(4'-sulfo-phenyl)-3-methyl-5-pyrazolone. 2½ parts of 10% sulfuric acid were added and 5 parts of wool yarn which had been thoroughly wet out was then introduced into the bath. 0.05 part of the abietamido propyl dimethyl hydroxy ethyl ammonium chloride were then added as a dyeing assistant and the bath brought slowly to a boil and maintained at the boil for sufficient time to complete the dyeing. The yarn was then removed and rinsed and dried. The dyeing was bright, level and of excellent color value.

A control dyeing obtained as in the preceding paragraph but omitting the surface active agent was noticeably inferior in brightness, levelness and strength of shade.

EXAMPLE 27

Lauramido dimethyl hydroxy ethyl ammonium chloride was prepared according to the method of Example 1 and used as a dye assistant according to the process described in Example 26. The shade obtained in the presence of this assistant was much superior to that obtained in its absence.

EXAMPLE 28

Stearamido propyl dimethyl benzyl ammonium chloride was obtained according to the method outlined in Example 1 and used as a dye assistant according to the process described in Example 26. A level dyeing was obtained in the presence of this reagent.

EXAMPLE 29

Lauramido propyl dimethyl benzyl ammonium chloride was prepared according to the method of Example 1 and used as a dye assistant according to the process of Example 26. The control dyeing in the absence of this reagent was quite skittery in appearance.

EXAMPLE 30

Decamido propyl dimethyl benzyl ammonium chloride was prepared by the steps outlined in Example 1 above, and then added to a dye bath according to the process described in Example 26. This product was equivalent as a dye assistant to the dye assistant utilized in Example 26 and gave markedly superior results over the control dyeing.

EXAMPLE 31

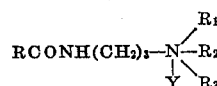
A 10 g. skein of wool dyed by the method described in Example 2 was divided into two equal 5-gram portions. One portion was immersed in a fresh bath containing 2 cc. of 10% sulfuric acid and 0.3 g. of gamma-stearamido propyl dimethyl hydroxy ethyl ammonium chloride in 300 cc. of water. After boiling in this solution for 1 hour, the shade of the wool skein so treated had been reduced by 50%. The second portion of wool yarn was immersed in a bath containing 2 cc. of 10% sulfuric acid

in 300 cc. of water and boiled for 1 hour. The reduction in shade was barely perceptible and illustrates clearly the advantage of these migratory agents for stripping.

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 basic nitrogenous fibers with metallized azo dyes soluble in acid baths, which comprises subjecting the material to be dyed to a dye bath containing a metallized azo dye, a water soluble acid and an amount sufficient to be effective but insufficient to cause scum formation and excessive precipitation in the bath of a gamma-alkyl amido propyl quaternary ammonium salt having the formula:



in which RCO— is an acyl radical selected from the group consisting of abietic acid and aliphatic fatty acids of from 10 to 18 carbon atoms; R₁ is selected from the group consisting of methyl, hydroxy ethyl and benzyl radicals; R₂ and R₃ are alkyl radicals of less than four carbon atoms and Y is the anion of an inorganic acid.

2. The method of claim 1 in which the quaternary ammonium salt is stearamido propyl dimethyl hydroxyethyl ammonium chloride.

3. The method of claim 2 in which the material to be dyed is wool, and the said wool passes directly from the spinning frames into the dye bath.

4. The method of claim 3 in which the dye bath contains an organic acid.

5. The method according to claim 4 in which said organic acid is formic acid.

6. The method according to claim 1 in which the quaternary ammonium salt is gamma-myristamido propyl trimethyl ammonium chloride.

7. The method of claim 6 in which the dye bath contains an organic acid.

8. A method according to claim 1 in which the quaternary ammonium salt is abietamido propyl dimethyl hydroxyethyl ammonium chloride.

9. A method according to claim 8 in which said acid is formic acid.

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

11. A method according to claim 1 in which the quaternary ammonium salt is gamma-stearamido propyl dimethyl benzyl ammonium chloride.

12. A method according to claim 11 in which said acid is formic acid.

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