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METACHROME DYEING WITH A COLLOIDIZED CATIONIC AGENT

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This invention relates to an improved dye composition for use in the metachrome dyeing process and to a method of dyeing therewith.

In the past there have been four general procedures employed in dyeing with metallizable dyes. The majority of metallizable dyes are azo dyes containing metallizable groups ortho to the azo group. There are, however, a few dyes which are not azo dyes such as certain anthraquinone colors which are also metallizable and they are included in the scope of the present invention. The first utilizes preformed metallized dyes and requires the formation of the metallized dyes before it is introduced into the dye bath. Practically all of the metallizable dyes may be utilized in this process but it is subject to a number of disadvantages. The dye is not very efficiently used, the dye bath is poorly exhausted, and the color value is not as high as desirable in some cases.

The second process is referred to as an "after chrome" procedure in which the fabric is dyed with metallizable dyes and then subjected to an after treatment with a solution of a compound of the metal to be introduced into the dye molecule. As the name implies the dye is applied the same as an acid color and it requires an extra process and extra time for the formation of the metallized complex.

The third procedure is the so-called "bottom chrome" process in which a metal compound is first deposited in the textile fiber and then the dye is applied and the metallized complex forms in the fiber. Here again this process is an extremely long one requiring several steps.

The fourth procedure is the so-called metachrome process in which the metallizable dye and the compound of the metal to be introduced are both present in the dye bath at the same time and the metallized dye is formed both in the fiber and in the bath itself and not introduced as a preformed compound.

The metachrome process presents many advantages. The dye is very effectively utilized when dyeing basic fibers such as the natural animal fibers, wool, silk, and the like or synthetic fibers of similar type from casein, polyamides and so forth. Certain dyes give good penetration and others do not. The dyes which do not give good penetration, particularly in the case of heavier shades have, therefore, been considered unsuitable for use in the metachrome process and have required resort to the process starting out with the preformed metallized dye, or the top or bottom chrome processes with their attendant disadvantages.

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It has been proposed to add cationic surface active agents to metachrome baths. Somewhat increased penetration into the individual fibers results but the cationic surface active reagent reacts with the acid groups of the metallizable dyes and the metal compound to form a water insoluble complex which tends to come down on the fabric or fiber to be dyed in the form of a scum resulting in streaky and non-uniform dyeing. For this reason, the use of the cationic surface active agents in a metachrome process for the dyeing of basic nitrogeneous fibers has been considered unsuitable.

The disadvantages of scum formation led to the development of an improved process described and claimed in the copending application of Millson and Royer, Serial No. 420,504, filed November 26, 1941, now abandoned, in which a non-ionic surface active agent was added to the bath to disperse the scum formation constituents. Even the improved process of the Millson and Royer application requires making up a special dye bath on the part of the dyer and rather careful control in addition to the added cost of the non-ionic surface active agent.

According to the present invention we have found that if the cationic surface active agent is colloidized with a mixture such as dextrin or the like no difficulty in scum formation is encountered. It is not necessary that the dyestuff be mixed with the surface active agent before colloidization as the same beneficial effect is obtained in either case.

The present invention is not limited to compositions in which the dye is already blended or both dye and mordant are blended as excellent results may be obtained by making up metachrome baths with the colloidized cationic surface active agent and the dyestuff separately.

It is an advantage that the present invention is very flexible where it is desired to produce a number of metachrome baths of the same dyestuff without varying amounts of cationic surface active agent so that different strengths of dyeing may be obtained. It is only necessary for the dyer to purchase the colloidized surface active agent and he can admix this with any desired portion of the chromable dyestuff and mordant. Where numerous short runs of different dyeing strengths are required this procedure has the marked advantage that it is not necessary for the dyer to stock a large number of blends of color and surface active agent. On the other hand,

where large runs of the same strength dyeing are required in many cases it is more convenient and more desirable for the dyer to buy a blend of the surface active agent and color with or without the mordant also blended so that all he has to do is to add water and make up a bath. This obviates any necessity of careful control of proportions and reduces the requirement for skilled supervision. It is also possible to assure absolute uniformity of composition because the dye manufacturer normally produces in large amounts and can standardize very thoroughly. It all cases the best compromise will be chosen in accordance with the particular requirements of the buyer.

In general, the colloidization of the cationic surface active agent may be effected by working it with a hydrophilic colloid such as a carbohydrate gum, that is, dextrine, polyvinyl alcohol, calcium lignin sulfonate, sodium lignin sulfonate, white tapioca dextrine, polyacrylamides, salts of polyacrylic acid, etc. Because of its cheapness and excellent working properties we prefer to use yellow corn dextrine. The working is in a stiff paste, for example, in a Werner-Pfleiderer dough mixer. The use of the term "colloidized cationic surface active agent" in the specification and claims is limited to such products which are colloidized with hydrophilic colloids. The colloidization as described above, and as will be more fully set out in the examples, results in the coating of the individual particles of the cationic surface active agent with a film of hydrophilic colloid which on careful drying and grinding produces a product of good autodispersibility and high total dispersibility. The word "colloidized" in the claims will be used in no other sense and particularly is not intended to cover mere fine dispersion of particles of the cationic surface active agent.

If desired the colloidization may be effected in the presence of deflocculating surface active agents although it is not necessary in all cases. It is, also, of importance that colloidized material which is desired in the dry form should be dried at a sufficiently low temperature, preferably in a vacuum dryer, so that the colloidized nature of the material is not destroyed and it retains a high degree of good autodispersibility and high total dispersibility.

It is not intended to limit the present invention to any particular theory and it has not as yet been determined definitely just why the colloidized cationic surface active agent will give high penetration in a metachrome bath without scum formation whereas when the cationic surface active agent is uncolloidized scum difficulties are encountered unless a non-ionic surface active agent is added.

The products of the present invention show good keeping qualities particularly when marketed in the dry form. Furthermore, the metachrome dyeing field is opened to a number of colors which formerly could not be used in this process or could not be used to produce deep shades. At the same time the advantages of the present invention are obtained without any costly added ingredients and without expensive processing.

Improved results are obtained with a large number of metallizable dyes. Sometimes the improvement is in strength and penetration and sometimes there is noted an improvement in levelness. With certain dyes improvements in both qualities are obtained.

The invention will be described in greater detail in conjunction with specific examples which show typical compositions and dyeing procedures according to the present invention. Unless otherwise stated all parts are by weight.

Example 1

1,000 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid are pasted with 200 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide (1 mole to 6 moles). These are then placed in a dough mixer and wet out with just enough water to give a thick plastic magma. This is worked for one hour in the mixer or until it gives a smooth homogeneous paste. The paste is then transferred to an enameled tray, placed in a vacuum dryer and dried at a temperature of about 70° C. with a vacuum of 28–29". When it has thoroughly dried, the product is ground and screened through a 140 mesh screen. This product is called the colloidized cationic agent. 60 parts of this colloidized cationic agent and 40 parts of the finely powdered red dye (C. I. 652) are dry blended until uniformly mixed. The resulting product is then dyed as follows:

Blended color—5% on weight of skein.
$(NH_4)_2SO_4$—10% on weight of skein.
$K_2Cr_2O_7$—1% on weight of skein.
Bath ratio—80–1.

The skein is first wet out by soaking in cold distilled water and then entered into the respective dye bath at approximately 120° F. The dye liquor is then raised to the boil gradually, in ½ hour, after which it is boiled for ½ hour with frequent turning of the skein to insure uniform dyeing. After 30 minutes boiling, ⅓% of 66° Bé. H_2SO_4 on the weight of the skein is added and the boiling continued for a second 30 minutes. At the end of this boiling period, ⅔% of 66° Bé. H_2SO_4 is added and the boiling continued for another half hour. The skein is then rinsed and air dried. The finished dyeing is red and has good fastness properties.

If an equivalent dyeing is made from the same dyestuff represented by C. I. 652 in which no colloidized cationic agent is present, and using the same dyeing procedure, the resultant dyeing is weak and commercially unsatisfactory.

Example 2

A dyeing of the blended color of Example 1 is made in the following dye liquor:

5% Blended color.
2% or less ammonium hydroxide to give a pH not greater than nine.
10% Epsom salts.
0.6% $K_2Cr_2O_7$.
80–1 Bath ratio (400 cc. water).

All percentages are based on the weight of the wool to be dyed.

A 5 gram wool skein is prewet with water, then entered into the dye bath at approximately 120° F. From this point on, the dyeing rates and additions of acid are similar to the dyeing procedure of Example 1 except 2% and 4% additions of 28% acetic acid are used instead of the ⅓% and ⅔% H_2SO_4.

The dyed skein is a rich deep red, very level dyed and generally superior to a dyeing of equivalent strength applied by the usual top chrome dyeing procedure.

Example 3

The preparation of the blended color and the dyeing procedure of Example 1 is repeated, except the color used is 1-amino-2-hydroxy-4-sulfo naphthalene diazotized and coupled to alpha naphthol (C. I. 201). The shade of the skein so dyed with the blended material containing the colloidized cationic agent is blue-black whereas the skein dyed with the color which has not been blended with colloidized cationic agent is a gray.

Example 4

The product of Example 3 is dye tested by the dyeing method used in Example 2. Here the improvement in color value is especially marked over that obtained from a dyestuff that has not been blended with colloidized cationic agent.

Example 5

The procedure of Example 1 is repeated except the color used in this example is 1-amino-2-hydroxy-4-sulfo-5 nitro naphthalene diazo coupled to alpha naphthol (C. I. 203). When dye tested by the procedure of Example 1, the product which has been blended with the colloidized cationic agent is definitely stronger and brighter than the dyeing obtained from the color which has not been blended with colloidized cationic agent.

Example 6

The procedure of Example 1 is repeated except the color in this example is 1-hydroxy-2-amino-4-nitro benzene diazo coupled to 6-sulfo-beta naphthol. When dye tested by the dyeing procedure of Example 1, the product which has been blended with the colloidized cationic agent gives a red-brown shade.

Example 7

The dyestuff of Example 6 is dye tested by the dyeing procedure of Example 2. The color is a beautiful rich brown having a fiber levelness very similar to that obtained by the top chrome dyeing procedure.

Example 8

The procedure of Example 1 is repeated using the color, C. I. 202, instead of the color used in Example 1. After colloidizing, blending and dye testing by the procedures of Example 1, the color value of the skein dyed with the colloidized material is a blue-black. If an equivalent dyeing is made from the same dyestuff represented by C. I. 202, in which no colloidized cationic agent is present, and using the procedure of Example 1, the resultant dyeing is a gray and not a blue-black.

Example 9

The procedures of Example 1 are repeated, except the color in this example is a dye having color index 274. The dyeings made with the colloidized cationic agent are strong, bright and more fiber level than the dyeings made from material which has no colloidized cationic agent present. This is especially true when the dyeing procedure of Example 2 is used.

Example 10

The composition of Example 8 is dye tested by the dyeing procedure of Example 1 except no acid additions are made. Even without the addition of acid, the color value of the dyeings is superior to those obtained under similar conditions when no colloidized cationic agent is present. The dye bath in which the colloidized product was used is better exhausted than the dye bath in which no colloidized cationic agent is present.

Example 11

A 5 gram wool skein is dyed with 5% of the color of Example 8, which has been blended with colloidized cationic agent, and 4% of a mordant containing 82.5% Epsom salts and 17.5% $K_2Cr_2O_7$. Both percentages are based on the weight of the wool. After the skein is entered at 120° F. the dyeing is carried out as in Example 1. The color value of the dye skein is a good blue-black having good fiber and fabric levelness.

Example 12

The procedure of the preceding example is repeated except sufficient ammonium hydroxide or equivalent ammonium salt is added to give an initial pH of 8.0–9.0 before the skein is entered. Then the dyeing is carried out as in the preceding example. The color value of the dyed skein is a rich strong blue-black having fiber and fabric levelness practically equal to that obtained from a top chrome dyeing.

Example 13

2 parts of the color (C. I. 652) and 3 parts of the colloidized cationic agent of Example 1 are dry blended. This is part "A."

35 parts of magnesium sulfate, 25 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid, 5 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide, and 7 parts of bichromate of potash are wet mixed in the Werner-Pfleiderer dough mixer until homogeneous. After vacuum drying and grinding, this product is known as part "B."

A composition is prepared from 5 parts of part "A" and 7 parts of part "B" to give a complete dyeing composition which contains all the active ingredients necessary to make a metachrome dyeing.

12% (on the weight of the wool) of the complete dyeing composition of this example are dissolved in 400 grams of water to which 2% of 28% ammonium hydroxide (also based on the weight of the skein) is added. A 5 gram wool skein prewet with water as in Example 1, is entered into the dye solution and dyed at the boil for 1½ hours with the addition of 4% of 8% of 28% acetic acid.

The color value of the resultant dyeing is good and the fastness properties are commercially satisfactory.

Example 14

1.25 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide are dissolved in an excess of ether. To this solution, 25 parts of Epsom salts are added, after which the ether is slowly evaporated on a steam table with constant stirring. The evaporation is completed in vacuo, then 1.5 parts of potassium bichromate (140 mesh) are added and the whole dry blended. This is product "A" of this example. Two parts of the commercial color known as C. I. 652 and 1 part of the condensation product of 2 moles of polyethylene oxide (molecular weight 4000) and 1 mole of the dimerized acid obtained by heat treating soyabean acids and distilling off the monomeric acids are dry blended. This is product "B" of this example.

10 parts of "A" and 2.7 parts of "B" are dry blended until a uniform mixture is obtained. This is product "C" of this example. A dyeing is made on a 5 gram skein by using 705 mg. of product "C" and 10 mg. of 28% NH_4OH in 400 cc.

of water. After the skein is entered, the dyeing is carried out as indicated in Example 2.

The skein, dyed with this product, is a bright red, and has excellent fastness properties.

Example 15

3 parts of the tertiary amine acetate prepared according to U. S. Patent 2,200,815 and 13 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid are wet out with a minimum of water to give a thick paste. These are colloidized as described in Example 1 after which the product is dried in a vacuum dryer at a temperature of about 70° C. It is dye tested as follows:

1 gram of the color known as 1-amino-2-hydroxy-4-sulfo-naphthalene diazotized and coupled to beta naphthol (C. I. 202) is dissolved in boiling water and made up to a liter. 100 cc. of this solution contains enough color to give a 2% dyeing on a 5 gram skein. The dye bath was prepared as follows:

100 cc. of this dissolved color, 300 cc. of water, 2% of 28% ammonium hydroxide, 3% of the colloidized cationic agent prepared in this example, 3.3% magnesium sulfate and 0.7% potassium bichromate is the dye-bath. All percentages are based on the weight of the skein.

A 5 gram woolen skein which has been pre-wet with distilled water was entered at approximately 120° F., brought to the boil in 30 minutes, boiled for 30 minutes, after which 2% of 28% acetic acid was added, boiling continued for 30 minutes, after which 4% of 28% acetic acid was added, and the boiling continued for another 30 minutes. At the end of this time, the dyeing made from the bath which contained the colloidized tertiary amine hydro acetate was a good strong blue-black color.

Example 16

5 parts of a cationic product believed to be cetyl or stearyl pyridinium halide and 25 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid are colloidized as described in Example 1 with the addition of 10 parts of water. After a smooth homogeneous mixture is obtained, this product is vacuum dried at a temperature of 70° C. and under vacuum of 27–28 inches. It is then dye tested with the same dye and by the same procedure as in Example 1, and a good strong blue-black dyeing is obtained.

Example 17

5 parts of a cationic agent believed to be the technical mixture of salt of quaternary ammonium bases containing the radicals $C_{15}H_{31}$ and $C_{17}H_{35}$ were colloidized using 25 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid and 6 parts of water as in Example 1. After the mixture has been well rubbed out on a glass plate to give a smooth uniform product, it was transferred to a vacuum dryer and dried at a temperature of 70° C. and a vacuum of 27–28 inches.

The product was then dye tested as in Example 1 and gave a strong blue-black color.

Example 18

5 parts of diethylamino ethyl stearyl amide acetate is processed similar to the product of Example 1 with 25 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid. It is then dye tested as in Example 1 giving a good, strong blue-black color.

Example 19

The procedure of Example 1 is repeated after first reacting the condensation product of the octadecyl guanidine bicarbonate and ethylene oxide with glacial acetic acid until the material is neutral to universal pH indicator paper. When this mixture has been colloidized, dried and ground, it can be substituted for the colloidized product of Example 1 and gives dyeing results similar to those obtained from the product of Example 1.

Example 20

400 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid, 100 parts of cerelose and 100 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide (1 mole to 6 moles) are worked in a dough mixer and wet out with just enough water to give a thick plastic magma. After this mixing is complete, the material is transferred to a vacuum dryer and dried at a temperature of about 70° C. This product can be substituted for that used in Example 1.

Example 21

100 parts of the cationic agent obtained by the condensation of octadecyl guanidine bicarbonate and ethylene oxide (1 mole to 6 moles) were colloidized using 400 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid as in Example 1. To this was dry blended 100 parts of urea. When 3 parts of this product are dry blended with 2 parts of the color obtained by diazotizing 1 amino-2-hydroxy-4-sulfo naphthalene and coupling to beta naphthol, C. I. 202, and dyed by the method used in Example 2, a good, strong blue-black color is obtained.

Example 22

5 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide (1 mole to 6 moles) and 5 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid were ground in a mortar with the addition of 10 parts water. A 2% dyeing of the dye, C. I. 202, was made from this paste with the dyeing procedure used in Example 1. A good blue-black dyeing is obtained.

Example 23

400 parts of corn dextrin made by dextrinizing corn starch with hydrochloric acid and 100 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide are worked in a dough mixer and wet out with just enough water to give a thick plastic magma. After this mixing is complete, the material is spread in thin layers in enameled trays and dried in a vacuum oven. After grinding and screening through a 140 mesh screen, 5 parts of this product is blended with 5 parts of the dye, C. I. 202.

A dyeing mordant is prepared by dry blending 82.5 parts of 140 mesh Epsom salts and 17.5 parts of 140 mesh $K_2Cr_2O_7$ or its chrome equivalent. Equal parts of the blended color and colloidized cationic surface active agent, and the mordant are then taken and a dyeing is made using 8% of the mixture based on the weight of the wool, adding NH_4OH to give a pH of 8.5 before the wool is entered. The dyeing is carried out with the addition of acetic acid as in Example 2. The dyeing obtained from this product is a bright, blue-black color having good fastness and levelness properties.

Example 24

5 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide, are colloidized using 25 parts of polyvinyl alcohol and sufficient water to give a stiff paste. The product is mixed and ground as in Example 15 and subsequently dried in vacuum at a temperature of 60–70° C. It is dye tested as follows:

100 milligrams of the dye, C. I. 202, are dissolved in 100 cc. of boiling water and transferred to a dyeing beaker. 150 milligrams of the colloidized cationic agent likewise is dissolved in hot water and added to the dye beaker. If desired, the color and the colloidized cationic agent can be admixed and dissolved at the same time. 500 milligrams of ammonium sulfate and 50 milligrams of potassium bichromate are then added to the dye beaker which is made up to a total volume of 400 cc.

A 5 gram woolen skein is prewet with water and entered into the dye bath at approximately 120° F., after which the dyeing is carried out as in Example 15.

The wool dyed with the dyestuff, C. I. 202, by this procedure has a strong blue-black shade, good fiber and fabric levelness and is commercially satisfactory.

Example 25

The procedure of the preceding experiment is repeated, except a high viscosity polyvinyl alcohol is used. This product can be substituted for the colloidized material of the preceding example and essentially the same results obtained after the wool has been dyed. If no colloidized cationic agent is present, the resultant dyeing is a gray.

Example 26

The procedure of the preceding example is repeated, except the polyvinyl alcohol is replaced by calcium lignin sulfonate. When this product has been dried and ground, it can be satisfactorily substituted for the colloidized material of Example 25. Sodium lignin sulfonate when substituted for calcium lignin sulfonate in this example gives equivalent results.

Example 27

The procedure of the preceding example is followed, except 250 parts of a 10% solution of water soluble methyl cellulose having a viscosity of 190 centipoises is used as the colloidizing agent instead of the calcium lignin sulfonate. When vacuum dried, this product formed a film. 3% (150 milligrams) of this film-like material was added to the dye bath and the dyeing carried out as in the preceding example, except no sodium lignin sulfonate was present. The resultant dyeing was not quite as strong as in the preceding example, but it was definitely a blue-black instead of the gray obtained when no colloidized cationic agent is present.

Example 28

The product of Example 1 is dyed on nylon by the method of Example 12. An excellent bright red shade is obtained which has good levelness.

Example 29

The product of Example 8 when dyed on nylon by the method of the preceding example, gave a bright, blue shade having good levelness.

Example 30

The composition of the preceding example is used, except the color is nitro amino phenol diazotized and coupled with meta phenylene diamine which is diazotized and coupled to 5-sulfonaphthol and the composition is dyed on a synthetic casein fiber. A level, brown dyeing having good fastness properties is obtained.

Example 31

The procedure of Example 2 is repeated except the color (C. I. 1085) is used instead of the red color of Example 2. A very level blue-black dyeing having excellent fastness properties is obtained.

From the foregoing examples it will be apparent that the present invention presents advantages with a large range of metallizable dyes. The advantages will vary with different dyes and in general some yellow dyes show less marked advantages than dyes of other shades.

We claim:

1. A colloidized mixture of hydrophilic colloid and cationic surface active agent having high total dispersibility and good autodispersibility and capable, when physically admixed with chromable dyestuff, of forming a metachrome dye bath giving deep color penetration into the fibers without objectionable scum formation.

2. A dye composition comprising a dry blend of chromable dyestuff and a colloidized mixture of hydrophilic colloid and cationic surface active agent, the colloidized mixture having high total dispersibility and good autodispersibility and the composition being capable of forming a metachrome dye bath giving a deep color penetration into the fibers without objectionable scum formation.

3. A dye composition comprising a dry blend of chromable dyestuff, a colloidized mixture of hydrophilic colloid and cationic surface active agent and a colloidized mordant containing a chromium compound and a hydrophilic colloid, the dry blend being capable of forming a metachrome dye bath by admixture with water without objectionable scum formation, the dyeing showing deep color penetration into the fibers.

4. A colloidized mixture of dextrine and cationic surface active agent having high total dispersibility and good autodispersibility and capable, when physically admixed with chromable dyestuff, of forming a metachrome bath giving deep color penetration into the fibers without objectionable scum formation.

5. A dye composition comprising a dry blend of chromable dyestuff and a colloidized mixture of dextrine and cationic wetting agent, the colloidized product having high total dispersibilty and good autodispersibility and the composition being capable of forming a metachrome dye bath giving deep color penetration into the fibers without objectionable scum formation.

6. A dye composition comprising a dry blend of chromable dyestuff, a colloidized mixture of dextrine and cationic surface wetting agent and a colloidized mordant containing a chromium compound and dextrine, the dry blend being capable of forming a metachrome dye bath by admixture with water without objectionable scum, the dye showing deep color penetration into the fibers.

7. A dye composition according to claim 1 in which the cationic agent is a condensation prod-

uct of octadecyl guanidine bicarbonate and ethylene oxide.

8. A dye composition according to claim 2 in which the cationic agent is a condensation product of octadecyl guanidine bicarbonate and ethylene oxide.

9. A dye composition according to claim 3 in which the cationic agent is a condensation product of octadecyl guanidine bicarbonate and ethylene oxide.

10. A dye composition according to claim 4 in which the cationic agent is a condensation product of octadecyl guanidine bicarbonate and ethylene oxide.

11. A dye composition according to claim 5 in which the cationic agent is a condensation product of octadecyl guanidine bicarbonate and ethylene oxide.

12. A dye composition according to claim 6 in which the cationic agent is a condensation product of octadecyl guanidine bicarbonate and ethylene oxide.

13. A method of dyeing by the metachrome process which comprises subjecting the material to be dyed to the action of a metachrome dye bath containing a chromable dyestuff, a colloidized mixture of a hydrophilic colloid and cationic surface active agent and a chrome mordant said dye bath being substantially free from added non-ionic surface active agents.

14. A method of dyeing by the metachrome process which comprises subjecting the material to be dyed to the action of a metachrome dye bath containing a chromable dyestuff, a colloidized mixture of dextrine and cationic surface active agent and a mordant, said dye bath being substantially free from added non-ionic surface active agents.

15. A method according to claim 13 in which the cationic surface active agent is a condensation product of octadecyl guanidine bicarbonate and ethylene oxide.

16. A method according to claim 14 in which the cationic surface active agent is a condensation product of octadecyl guanidine bicarbonate and ethylene oxide.

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