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METACHROME DYEING PROCEDURE

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This invention relates to improved metachrome dyeing processes.

In the past there have been four general procedures employed in dyeing with metallizable dyes. The first utilizes preformed metallized dyes and requires the formation of the metallized dye 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" or "top 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 dye, 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 start 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. However, in many cases the dye is not effectively utilized when dyeing basic nitrogenous 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 uniform fiber penetration in a yarn, and others penetrate only some of the fibers. The dyes which do not penetrate all of the fibers or are destroyed during the dyeing operation, 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.

According to the present invention it is found that markedly increased strength and levelness of

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dyeing is obtained if three factors are present in the process. These three factors are:

1st: The presence of a salt of an alkaline earth metal.

2nd: A water dispersible surface active composition containing at least one cationic surface active agent.

3rd: The pH of the dye bath is sufficiently high initially so that rapid chromation is prevented or retarded, and during the dyeing process the pH is progressively lowered until final chromation results.

With certain dyes any one of the three factors referred to above will effect some improvement either in color value or levelness, but with certain other dyes, both of these improvements in dyeing characteristics are not obtained with metallizable dyes unless all three of the above reaction conditions are present, and the present invention contemplates only processes in which all three factors are effective.

The alkaline earth metal salts or salts to be used are not in the least critical. Any of the common soluble salts may be used. The different alkaline earth metal salts will vary to some extent in their effect, and this variation is not the same with all metallizable dyes. In general, best results are obtained with magnesium salts, magnesium sulfate being particularly desirable, by reason of its cheapness, ready availability and the excellent results which it gives in the process of the present invention. Accordingly magnesium sulfate represents the preferred alkaline earth metal salt, though in its broader aspects the invention is not limited to its use.

The reason for the improved results obtainable with alkaline earth metal salts, and particularly the increased strength of dyeing which follows their use, has not been completely determined and, therefore, the present invention is not intended to be limited to any theory of the action of the alkaline earth metal salts. Certain observations with certain dyestuffs make it appear very probable, that at least with some dyestuffs, magnesium or the other alkaline earth metal salts actually form metal complexes with the dye, which complexes are only stable in solutions of high pH. Some of the dyes change their color very strikingly when they are introduced into a dye bath containing the alkaline earth metal salt. Such a great change in color, which is again reversed as the dyeing proceeds and the pH falls to sufficiently low values, makes it almost certain that there is an actual chemical change in the dye molecule. The conditions un-

der which this color change takes place with some of the metallizable dyes make it probable that the alkaline earth metal salt actually forms a dye complex which is then decomposed when the pH falls to a sufficiently low value. This explanation is consistent with the relatively strong basic character of the alkaline earth metal salt which would make it probable that if a complex is formed, it would not be acid stable. The above explanation is advanced, therefore, as probable in the case of some at least of the metallizable dyes which may be used in the process of the present invention.

It is an advantage of the invention that the amount of the added alkaline earth metal salts is not critical. It should, however, be realized that the action appears to be in no sense catalytic. Relatively substantial amounts of alkaline earth metal salt must be added. Normally the amount added is at least equal to the weight of the dye, although this figure does not represent a sharp or critical dividing line. Smaller amounts will exert an effect, but one which rapidly diminishes as the amount of salt becomes inadequate. It has been found that the amount of alkaline earth metal salt may be advantageously correspondingly greater than the weight of the dyestuff. For example, the use of five times as much alkaline earth metal salt gives excellent results, and since the alkaline earth metal salts are relatively cheap chemicals, it is preferred to use them in excess of the weight of the dyestuff, although the invention is not broadly limited to this preferred amount.

The second factor requires a water dispersible surface active composition containing at least one cationic surface active agent. It is also desirable that any insoluble reaction products of the cationic surface active agent be likewise dispersible. This dispersibility of the surface active composition may be effected in several ways. For instance, the cationic surface active agent may be colloidized either by itself or in combination with the dyestuff or alkaline earth metal salt or with the chromating mordant. These methods are described in Patent No. 2,434,178 issued January 6, 1948 to Royer and Amick. Another method of obtaining water dispersibility is to associate the cationic surface active agent with nonionic surface active agents as is described in the Millson and Royer application Serial No. 420,504, filed November 26, 1941.

The present invention is not concerned with the particular methods of achieving dispersibility of the surface active component, this forming the subject matter of the applications above referred to. On the contrary, the present invention is concerned only with water dispersible cationic surface active compositions when associated with the other two factors of the process of the present invention, namely, the presence of the alkaline earth metal salt and the initial high pH of the dye bath.

The third factor, namely, high initial pH, is also not a critical operating procedure. It will vary quite widely with different dyestuffs and with different fabrics. In general it will never be lower than 5.5 and the upper limit is from about 8 to 9.5. The upper limit is defined, not so much by the reaction itself, as by the fabric, because it is necessary to maintain the pH below the point at which the basic nitrogenous fibers are injured. In general, the initial pH should be chosen sufficiently high to retard initial chromation. With dyestuffs with which it seems probable that a complex is formed with the alkaline earth metal salt, the pH initially should be high enough so that the complex, if there be one present, is not decomposed until the dyeing of the fiber has proceeded to the desired extent.

As the fibers are dyed and the normal heating of the bath continues, there is a definite lowering of pH, the bath becoming more and more acid. When the pH gets low enough, both dyeing and chromation proceed more rapidly, and a final dyeing of high strength and good levelness results. Thus it is now possible to obtain deep shades, such as a deep chrome black, by a true metachrome process.

While, as pointed out above, the pH of the dye bath is lowered by the dyeing procedure itself, probably because of a reaction of the basic nitrogenous fiber with the alkali present, this lowering is usually insufficient, hence in the majority of cases it is desirable to add small amounts of acid or acid salts as the dyeing proceeds. Preferably the acid is added in parts—⅓ after one-half hour boiling, and ⅔ after an hour's boiling. The exact amount of addition of acid and the time and portions are not critical, but optimum results will vary a little with different colors. This is entirely consistent with normal dyeing practice where it is usually necessary to make some changes in the dyeing time, temperature, and pH with different dyes and different fibers in order to get the best results. The same type of adjustment is employed in the process of the present invention which is an advantage as the dyer does not have to learn new techniques.

While the process of the present invention gives important improvement in dyeing with ordinary dyes by the metachrome method, producing strong shades with a high degree of levelness and excellence of fastness to light and fulling, a further advantage lies in the fact that certain chromable dyes, which are dyeable in the metachrome process only when the wool has been modified by one of the various non-felting treatments such as chlorination, can be dyed by the present process on ordinary wool. This is important as it opens up a new field for these dyes. In addition to the improved results obtained by the process of the present invention, a further advantage lies in the material saving which can be effected in the amount of chromium containing salt used. In favorable cases this may amount to 40 or 50%.

The invention will be described in greater detail in conjunction with the following specific examples. The parts are by weight.

Example 1

One part of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide (1 mole to 6 moles) are dissolved in an excess of organic solvent, e. g., ether. 20 parts of Epsom salts are added and the ether evaporated slowly with constant stirring to deposit the cationic agent on the Epsom salts base. Finally the product is vacuum dried. When the drying is completed, the product is grindable. 52.5 parts of this product is dry-blended with 3 parts of powdered $K_2Cr_2O_7$ to give a mordant. Twelve percent of this product (based on the weight of the wool) is used with 2% of the ordinary commercial chrome types to give a satisfactory dyeing. The dyeing is made as follows:

2% dye (C. I. 202) predispersed in boiling

water was admixed with 12% of the mordant and a sufficient amount of ammonia or ammonia and ammonium salt such as ammonium dihydrogen phosphate, to produce a pH of about 8.5 to 9.0 in a 400 cc. volume, sufficient water being used to make the necessary dilution.

A 5 gram woolen piece or skein is pre-wet with water and entered into the dye bath at 120° F. The dye liquor is gradually brought to the boil in ½ hour with frequent turning of the wool to insure uniform dyeing. Boiling and turning are continued for ½ hour, after which 2% of 28% acetic acid is added. After another half-hour on the boil, 4% of 28% acetic acid is added. Dyeing is continued at the boil for a third half-hour making a total dyeing time of two hours. The color of the dyed skein is blue-black and the dyeing has good fastness and is very level. Ordinarily this color can be dyed satisfactorily only by the very cumbersome top or bottom chrome method.

Example 2

37.5 parts of corn dextrine made by dextrinizing corn starch with hydrochloric acid, 37.5 parts of Epsom salts, 3.75 parts of the cationic agent of Example 1, 4.5 parts of $K_2Cr_2O_7$ and about 20 parts of water are wet-blended in a Warner-Pfleiderer mixer until uniform. This gives a thick plastic magma. The product is then transferred to enameled trays and dried in a vacuum dryer, ground and screened through a 140 mesh screen. 12% of this product is substituted for the material in Example 1 and dyeings are carried out in the same way with essentially the same results.

The chrome equivalent amount of K_2CrO_4 can be used in place of the $K_2Cr_2O_7$.

Example 3

The product of Example 2 is used in making a dying of the dye C. I. 652, using the dyeing formula of Example 1. This dye gives an excellent color value which is superior to that obtained by ordinary metachrome dyings or even top chrome dyeings.

Example 4

500 parts of the dextrine of Example 2 and 100 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide (1 mole to 6 moles) are blended in a Werner-Pfleiderer mixer with sufficient water to give a stiff plastic magma. The well mixed material is then transferred to enameled trays and vacuum dried. It is then ground and screened through a 140 mesh screen. 30 parts of this product, 24 parts of 100 mesh Epsom salts, and 6 parts of 140 mesh $K_2Cr_2O_7$ are dry-blended to give a mordant. 6% of this mordant and 2% of 28% NH_4OH (both on the weight of the wool) and 100 mg. of the dye having C. I. 203 are dyed on a 5 gram woolen skein as in Example 1. The dyeing obtained is blue-black, has excellent fastness properties and is fiber level.

Example 5

37.5 parts of the dextrine of Example 2, 37.5 parts of Epsom salts, 3.75 parts of a condensation product of octadecyl guanidine bicarbonate and ethylene oxide (1 mole to 6 moles), 4.5 parts of potassium bichromate and about 20 parts of water are added to a Werner-Pfleiderer mixer and worked until homogeneous. A thick plastic magma is produced which is transferred to enameled trays, dried in the vacuum dryer, ground and screened through a 140 mesh screen producing a colloidized mordant.

A dye bath is prepared as follows:

0.1 g. dye (C. I. 202) predispersed in boiling water, approximately 2% of 28% NH_4OH to give a pH not greater than 9.5
12% colloidized mordant
400 cc. dye bath volume

A 5 gram woolen piece or skein is pre-wet with water and entered into the dye bath at 120° F. The dye liquor is gradually brought to the boil in ½ hour with frequent turning of the wool to insure uniform dyeing. Boiling and turning are continued for ½ hour after which ⅓% of H_2SO_4 is added. Dying is continued at the boil for a second half hour, after which ⅔% of H_2SO_4 is added. Dyeing is then continued for a third half-hour at the boil making a total dyeing time of two hours.

The color of the dyed skein is blue-black and the dyeing has good fastness and is fiber level. Ordinarily this color can be dyed satisfactorily only by the very cumbersome top or bottom chrome method.

The same results are obtained if the potassium bichromate is substituted by a chromium equivalent amount of potassium chromate.

Example 6

The dyeing procedures of the preceding example is repeated using the dye C. I. 652 instead of the dye of Example 5. The dye gives an excellent color value which is superior to that obtained by ordinary metachrome dyeings or top chrome dyeings.

Example 7

500 parts of the dextrine of Example 2 and 100 parts of the cationic surface active agent described in Example 5 are colloidized in a Werner-Pfleiderer mixer with just sufficient water to give a stiff plastic magma. The product is then dried, ground and screened as described in Example 5. 30 parts of the screened material are dry-blended with 100 parts of Epsom salts and 6 parts of potassium bichromate.

A dye bath is prepared with 13.5% of the above mordant and 2% of 28% ammonia (both on the weight of the wool) and 2% of dye having C. I. 203 are added, and the dyeing is carried out by the procedure of Example 1 or Example 5. The dyeing produces a blue-black shade which is fiber level and has excellent fastness properties.

Example 8

A dye bath is prepared as described in Example 4 using 7% of mordant and 6% of dye. Wool is dyed in the bath and builds up with the increased amount of color to give a very dark, blue-black shade of excellent fastness properties and fiber levelness.

Example 9

500 parts of the dextrine of Example 2 and 100 parts of cationic surface active agent as described in Example 7 are colloidized and vacuum dried. 30 parts of the product are blended with 35 parts of 100 mesh Epsom salts and 8.3 parts of potassium bichromate until a uniformly blended product is obtained.

7% of the mordant produced and 2% of 28% ammonia together with 2% of the dye C. I. 292 are made into a dye bath. Wool is dyed in skein form as described in the foregoing examples, and a strong green dyeing is obtained having excellent fastness properties.

Example 10

2 parts of the dye C. I. 274, and one part of the condensation product of 2 mols of polyethylene oxide (molecular weight 4000) and 1 mol of the dimerized acid obtained by heat treating soya bean acids and distilling off the monomeric acids are dry blended. 3% of this product, 6% of the mordant of Example 4 and 2% of 28% ammonia are dissolved in 400 parts of water and wool is dyed therein by the procedure of Example 1. A good, bright orange color is obtained and the dyed wool has good fastness and levelness.

Example 11

A dye bath is prepared with 1 part of the dye having the Color Index #203 (pure presscake) dispersed in 2000 parts of boiling water. This is then diluted with an equal amount of water containing 6 parts of the mordant of Example 4 and 2 parts of 28% ammonia. Fifty parts of pre-wet wool are then entered and dyed as in Example 5. A black shade of good fiber levelness is obtained.

Example 12

The procedure of Example 4 is repeated, except the dyeing is made on synthetic casein fiber and the dye is nitro amino phenol diazotized and coupled with meta phenylene diamine which is diazotized and coupled to 5-sulfo α-naphthol, Prototype 14. An excellent brown dyeing is obtained.

Example 13

The procedure of Example 4 is repeated, except the dye is C. I. 652 and the material is nylon. A strong, bright red shade is obtained.

Example 14

The procedure of the preceding example is repeated except the dye is C. I. 292. A good slate green shade is obtained which is commercially satisfactory.

Example 15

50 parts of the dextrine of Example 2 and 10 parts of the condensation product of octadecyl guanidine bicarbonate and ethylene oxide (6–1) are colloidized and vacuum dried. This product is then ground, screened through a 100 mesh screen, and dry blended with 40 parts of the commercial dye having Color Index No. 203.

A batch of woolen fabric is dyed in a commercial dye kettle as follows:

10% of the above blended color
6% ammonium acetate
3.3% Epsom salts
0.7% potassium dichromate

The cloth was entered into the dye kettle, and wet out with water. If necessary, the cloth is treated to make it neutral, after which the treating water was discharged from the kettle, refilled, heated to 120° F. and the above ingredients added in the order given. The starting pH was about 5.5 as determined by Universal indicator paper. The dye liquor was slowly heated to 207° to 208° F. at which time the pH was about 6.0 and run about 40 minutes, after which 2% of 28% acetic acid was fed on and the pH dropped to 5.0. After dyeing for an additional 40 minutes, 2% of 28% acetic acid was added a second time, and the pH remained about 5.0.

When the dyeing was completed, the woolen fabric was dyed a black color having good fastness and levelness.

Example 16

A dyeing composition is prepared by dry blending 60 parts of the colloidized cationic surface active agent of the preceding example with 40 parts of the yellow dyestuff prepared by diazotizing sulfanilic acid and coupling to 2-hydroxy-5-amino benzoic acid.

A dyeing is prepared as follows:

All weights are based upon the weight of the wool to be dyed
5% of the blended dye prepared as in the preceding paragraph
10% ammonium sulfate
0.6% potassium dichromate
Bath ratio: 80–1

The starting pH of this dye solution will vary from a pH of 5.0–6.0 depending upon the previous history of the wool and how thoroughly it has been neutralized after the preceding operation.

The bath is brought to the boil gradually in 30 minutes, boiled 30 minutes, after which 3% of the 28% acetic acid is added. After an additional 30 minutes at the boil, a second addition of 3% of 28% acetic acid is added and the boiling continued for another 30 minutes.

Wool dyed as above has a brilliant yellow color, showing excellent levelness and good fastness properties.

Example 17

The procedure of Example 1 is repeated except the dye C. I. 1085 is used instead of C. I. 202 of Example 1. The dyeing produces a blue-black shade which is level and has excellent fastness properties.

Example 18

A dye bath is prepared as follows, all weights being based on the wool.

2% dye having Color Index No. 202
2% of 28% ammonium hydroxide
1% of the non-ionic agent prepared by reacting 2 moles of poly-ethylene oxide (M. W. 4000) and 1 mole of the dimerized acid obtained by heat treating soya bean acids and distilling off the monomeric acid
0.5% of the cationic active agent of Example No. 1
10% Epsom salts
0.6% potassium dichromate

The dye bath is then made up to 400 cc. with water, after which a 5-gram woolen piece or skein is pre-wet and dyed as in Example No. 1 or No. 5 and the strength and shade of the dyed piece is generally like that obtained from Example No. 1

Example 19

The procedure of Example No. 18 is repeated except the dye having Color Index No. 652 is used instead of the dye having Color Index No. 202. Wool dyed by this color and procedure gives excellent strength and levelness, usually superior to the conventional topchrome methods of dyeing.

Example 20

The procedure of Example No. 18 is repeated except the dye having Color Index No. 98 is used in place of the dye having Color Index No. 202. Wool dyed by this color and procedure has excellent strength and fiber levelness, being equal usually to a top chrome dyeing as made by the conventional methods.

Example 21

The procedure of Example No. 18 is repeated except the dye having Color Index No. 1085 is used in place of the dye having Color Index No. 202. Wool dyed by this color and procedure has good color value and fiber levelness.

Example 22

The procedure of Example No. 18 is repeated except the dye having Color Index No. 201 is used in place of the dye having Color Index No. 202. Wool dyed by this dye and procedure is stronger and brighter than wool dyed with an equivalent amount of dye which is dyed by the conventional top chrome procedure.

Example 23

The procedure of Example 18 is repeated except the dye having Color Index 274 is used in place of the dye having Color Index No. 202. Wool so dyed has excellent color value, is bright and has good fiber levelness.

Example 24

400 parts of yellow corn dextrine and 100 parts of the cationic surface active agent described in Example 1 are intimately mixed and vacuum dried as described. 5 parts of this material are then dissolved in 95 parts of water to give a 1% solution of the cationic surface active agent. A dye bath is then prepared as follows:

2% of the dye having Color Index No. 203 predissolved in 100 ml. water
300 ml. of water
2% of 28% ammonium hydroxide
2.5 ml. of the 1% solution of cationic surface active agent described above.
10% Epsom salts
0.6% potassium bichromate

A 5-gram pre-wet wool skein is then dyed therein, using the dyeing procedure on Example No. 1 and the strength and shade of the dyed wool is very fiber level and is usually stronger than equivalent dyeings made by the conventional top chrome procedure. Magnesium acetate or magnesium chloride may be substituted for the Epsom salts.

The addition of the ammonium hydroxide generally changes the pH to 9–9.6 depending upon the pH of the water added to the dyebath. The shade of the dye having Color Index No. 203 is plum colored or reddish after the addition of the water to make up the dyebath, particularly if distilled water having a pH lower than 7 is used. After the addition of the ammonium hydroxide, the shade of this color becomes greenish-blue. Upon the addition of the Epsom salts the color of the dye solution becomes a cherry red, although there is no appreciable change in pH. During the subsequent dyeing, this dyebath exhausts very rapidly, much more so than when a similar dyeing is made except the Epsom salts is omitted.

Example 25

The procedure of Example 24 is repeated, except 10% of calcium nitrate .4 H_2O is substituted for the Epsom salts of Example 24. The shade of the dyed wool is slightly grayer than that obtained when Epsom salts is used. The addition of 10% of the calcium nitrate .4 H_2O based on the weight of the wool to the dyebath likewise caused no appreciable change in pH but did cause the blue green shade of the dye solution to become a brighter red.

Example 26

The procedure of Example 24 is repeated except 10% of barium nitrate is used instead of the Epsom salts. The wool dyed from this bath is slightly bluer and brighter than that dyed by the procedure of Example 24.

Example 27

The procedure of Example 25 is repeated except the dye having Color Index No. 652 is used instead of the dye having Color Index No. 203. A good strong red dyeing is obtained. If desired, the calcium nitrate may be replaced with strontium chloride.

Example 28

The procedure of Example 18 is repeated exactly except 0.5% of the surface active agent, tertiary amine hydroacetate, prepared according to U. S. P. 2,200,815 is used instead of the surface active agent prepared by the condensation of octa decyl guanidine bicarbonate and ethylene oxide (6:1) which was used in Example 2. Wool dyed with this procedure shows good strong blue-black color with good penetration.

Example 29

The procedure of the preceding example is followed exactly except the surface active agent, cetyl pyridinium chloride, is used instead of the tertiary amine hydroacetate of the preceding example. A good strong bright blue-black dyeing is obtained.

Example 30

The procedure of the preceding experiment is repeated except the surface active agent, cetyl trimethyl ammonium bromide is used instead of the cetyl pyridinium chloride. A good strong bright blue-black dyeing is obtained.

Example 31

The procedure of Example 18 is repeated exactly except the surface active non-ionic agent of Example 18 is replaced by 1% of beta hydro-triethoxy-propyl-lauramide. A good bright blue-black dyeing which showed excellent penetration is obtained.

Example 32

The procedure of the preceding example is repeated exactly except the beta-hydro-triethoxy-propyl-lauramide is replaced with 1% of p-hexadecyl phenyl ether of polyethylene glycol.

Example 33

The procedure of Example 18 is repeated except the non-ionic surface active agent of Example 18 is replaced with the condensation product of stearyl alcohol with 8 moles of ethylene oxide liquified with 30% H_2O. Wool dyed by this procedure gives a bright blue-black shade showing excellent penetration and good fiber levelness.

Example 34

The procedure of Example 18 is repeated except the non-ionic surface active agent of Example 18 is replaced with 1% of hexa-ethylene glycol dodecyl amino triazine resin. The strength obtained with this combination is not as good as with the combination of Example 18 but is much superior to the results obtained when no surface active agents are present.

In the specific examples no additional chromium compound is added during the dyeing. In the production of most shades particularly lighter

shades, this gives the best results. However, in some cases, particularly with dark shades such as maroon, brown, navy and black, it is sometimes advantageous to add small amounts of additional bichromates, for example, .3 to .5%, to the bath after it has been boiling for about one-half hour or so. The additional chromium makes the dark shades somewhat richer and in many cases improves fastness to wet finishing. The addition of small amounts of the chromates to the bath after the dyeing has proceeded for some time is therefore included in the scope of the present invention.

The improved results obtainable by means of the present invention are not always the same with each dye. In many cases improved strength and penetration result: in other cases, the levelness is better while with some dyes, improvements in both characteristics are observed. The degree of improvement in various characteristics varies with the dye. In general, the process of the present invention shows less marked advantages with some yellow dyes than with dyes of other shades.

In the examples, dyestuff mixtures have been colloidized by working in a relatively stiff paste with carbohydrates such as dextrine and dried at a low temperature so that the individual particles on contact with water dispersed rapidly without violent agitation to form a colloidal solution. Such products have been described in the specification as "colloidized." This term is used in the claims in no other sense.

We claim.

1. A method of dyeing which comprises subjecting substantially unmetallized basic nitrogenous fibers to the action of a dye bath formed by mixing a chromable dye, a soluble chromium containing salt, a soluble alkaline earth metal salt, a water-dispersible surface-active composition containing at least one cationic surface active agent, water, and sufficient alkali to make the bath alkaline and to cause said dye to react with said alkaline earth metal salt to form an alkaline earth metal complex of said dye and insufficient to materially damage the fibers, partially dyeing said fibers from said complex, gradually lowering the pH of said bath to a point where decomposition of said complex and chromation take place, and completing the dyeing at said lowered pH.

2. A method of dyeing which comprises subjecting substantially unmetallized basic nitrogenous fibers to the action of a dye bath formed by mixing a chromable dye, a soluble chromium containing salt, magnesium sulfate, a water-dispersible surface-active composition containing at least one cationic surface active agent, water, and sufficient alkali to make the bath alkaline and to cause said dye to react with said alkaline earth metal salt to form an alkaline earth metal complex of said dye and insufficient to materially damage the fibers, partially dyeing said fibers from said complex, gradually lowering the pH of said bath to a point where decomposition of said complex and chromation take place, and completing the dyeing at said lowered pH.

3. A method of dyeing which comprises subjecting substantially unmetallized basic nitrogenous fibers to the action of a dye bath formed by mixing a chromable dye, a soluble chromium containing salt, a soluble alkaline earth metal salt, a water-dispersible surface-active composition containing at least one cationic surface active agent, water, and sufficient alkali to make the bath alkaline and to cause said dye to react with said alkaline earth metal salt to form an alkaline earth metal complex of said dye and insufficient to materially damage the fibers, partially dyeing said fibers from said complex, gradually lowering the pH of said bath by the addition of successive small portions of acid to a point where decomposition of said complex and chromation take place, and completing the dyeing at said lowered pH.

4. A method of dyeing which comprises subjecting substantially unmetallized basic nitrogenous fibers to the action of a dye bath formed by mixing a chromable dye, a soluble chromium containing salt, magnesium sulfate, a water-dispersible surface-active composition containing at least one cationic surface active agent, water, and sufficient alkali to make the bath alkaline and to cause said dye to react with said alkaline earth metal salt to form an alkaline earth metal complex of said dye and insufficient to materially damage the fibers, partially dyeing said fibers from said complex, gradually lowering the pH of said bath by the addition of successive small portions of acid to a point where decomposition of said complex and chromation take place, and completing the dyeing at said lowered pH.

5. A method of dyeing which comprises subjecting substantially unmetallized basic nitrogenous fibers to the action of a dye bath formed by mixing a chromable dye, a soluble chromium containing salt, a soluble alkaline earth metal salt, a water-dispersible surface-active composition containing at least one cationic surface active agent, water, and sufficient alkali to make the bath alkaline, but with a pH not greater than 9.5, and to cause said dye to react with said alkaline earth metal salt to form an alkaline earth metal complex of said dye and insufficient to materially damage the fibers, partially dyeing said fibers from said complex, gradually lowering the pH of said bath to a point where decomposition of said complex and chromation take place, and completing the dyeing at said lowered pH.

6. A method of dyeing which comprises subjecting substantially unmetallized basic nitrogenous fibers to the action of a dye bath formed by mixing a chromable dye, a soluble chromium containing salt, magnesium sulfate, a water-dispersible surface-active composition containing at least one cationic surface active agent, water, and sufficient alkali to make the bath alkaline, but with a pH not greater than 9.5, and to cause said dye to react with said alkaline earth metal salt to form an alkaline earth metal complex of said dye and insufficient to materially damage the fibers, partially dyeing said fibers from said complex, gradually lowering the pH of said bath to a point where decomposition of said complex and chromation take place, and completing the dyeing at said lowered pH.

7. A method according to claim 1 in which the cationic surface active agent is a condensation product of octadecyl guanidine and ethylene oxide.

8. A method according to claim 2 in which the cationic surface active agent is a condensation product of octadecyl guanidine and ethylene oxide.

9. A method according to claim 4 in which the cationic surface active agent is a condensation product of octadecyl guanidine and ethylene oxide.

10. A method according to claim 6 in which the cationic surface active agent is a condensation

product of octadecyl guanidine and ethylene oxide.

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