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PROCESS FOR DYEING FABRIC

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This invention relates to materials of high molecular weight containing nitrogen and to the process of preparing them. It relates more particularly to products obtained by the interaction of a water-soluble polymeric amide, an aldehyde and an amine. It also relates to the use of the products thus obtained in fixing dyes on fabrics, particularly acid dyes on cellulosic fabrics. It further relates to the use of these products in dyeing leather and also in the filling of leather.

The products formed by the interaction of a polymeric amide such as polymethacrylic amide, an amine such as dimethylamine, and an aldehyde such as formaldehyde are all high molecular weight substances containing nitrogen. They are soluble in water and form with acid dyes and with natural, synthetic and mineral tanning agents, compounds which are insoluble in neutral and acid aqueous solutions. On account of these properties the new products are useful in dyeing fabrics, particularly cellulosic fabrics, and leather. They are also useful in the process of tanning because the insoluble products which they form with the tanning agents can be easily formed within the leather, thus yielding a good, full leather.

It is known that cellulosic fabrics cannot be dyed directly with acid dyes. Many methods have been proposed for treating fabrics or fibers of this kind with basic substances so as to introduce basic groups into the cellulose molecule. This is important because very often it is desirable to weave fabrics from two or more fibers, for example cotton and silk. Such fabrics cannot be dyed with a single dye to a uniform color. If basic groups are added to the cellulose molecule, then acid dyes can be used on mixed fabrics and uniform color obtained. Processes for treating cellulose so as to introduce such groups include treatment with ethylene imine, epichlorhydrine followed by ammonia, impregnation with urea-formaldehyde condensation products, etc. These all have the disadvantage that the fabric must be subjected to a separate treatment to prepare it for dyeing with acid dyes. When using the products of the present invention for the purpose of fixing acid dyes on cellulosic fabrics, it is only necessary to impregnate the fabric with a solution of the condensation product and then treat the fabric with a solution of an acid dye. By means of this treatment the dye is bound in the fiber. In some cases very uniform dyeings can be achieved by first impregnating the fabric, either hot or cold, with the products of this invention, wringing out, drying at a temperature of 40 to 50° C., and then applying the dye. In many cases it is advantageous to dry the impregnated fabric at higher temperatures, for example about 100° C. before dyeing.

When dyeing fabrics, leather or other fibrous material, the dye may be applied first, followed by treatment with the high molecular weight nitrogenous products for the purpose of fixing the dye on the fiber. The lightfastness of such dyeings is much better than when the treatment with the new products is omitted.

When used for filling leather, the new condensation products have many advantages over the usual fillers such as kaolin, calcium carbonate, etc. These are usually drummed into the leather along with the fat liquor. The new products on the other hand may be added before the fat liquor and, since they form insoluble products with the tanning agent, the actual filling material is formed directly in the leather. A single treatment of the leather with these materials gives an improved product but still greater improvement is attained by using relatively large amounts of the new products and then subjecting the leather to a second tanning treatment. By this means more of the insoluble complex can be incorporated and a fuller leather obtained.

The nitrogenous products of high molecular weight with which the present invention is concerned are prepared by reacting a polymeric amide such as polymethacrylamide, an amine such as dimethylamine, and an aldehyde such as formaldehyde in an acid, neutral or alkaline medium. It is preferable, however, to carry out the reaction in a slightly acid medium in which case the amine is employed in the form of one of its salts.

The amines which can be used in preparing these condensation products are those which have at least one hydrogen atom attached to the amino nitrogen atom. Examples of such amines are monomethylamine, dimethylamine, the primary and secondary ethyl, propyl, butyl and higher aliphatic amines, carbocyclic amines such as benzylamine, cyclohexylamine, naphthylamines, phenylenediamines, and heterocyclic amines, such as piperidine. When these compounds are insoluble or difficultly soluble in water they are used in the form of their salts, for example, the hydrochlorides. Other compounds containing an —NH_2— or —NH— group, for example, amino acids, may also be used in the reaction.

Formaldehyde is preferred for condensing with

the polymeric amide and the aliphatic amines or amino acids. It may, however, be replaced by other aldehydes such as furfurol, acrolein, acetaldehyde, crotonaldehyde, etc. These aldehydes are advantageously employed in place of formaldehyde in cases where the latter forms insoluble compounds with the amine, as for example with phenylenediamine hydrochloride or β-naphthylamine hydrochloride.

The polymeric amides are those obtained by polymerizing such compounds as methacrylic amide, acrylic amide, and other similar, unsaturated acid amides. Polymethacrylic amide is particularly suitable. It is preferable to employ polymers which yield aqueous solutions of low to intermediate viscosity because, if solutions of high viscosity are employed, difficulties in handling may arise. Joint polymers of the unsaturated acid amides and other polymerizable materials such as acrylic, methacrylic and vinyl esters may be employed, in which case care should be taken that the joint polymer contains a sufficient proportion of amido groups to render it soluble in water. Water-soluble materials obtained by the partial alkaline hydrolysis of polymeric acid nitriles, such as polyacrylic nitrile may also be used provided they contain a sufficient proportion of amido groups. Such compounds probably contain unchanged nitrile groups as well as some carboxyl groups. Such compounds may be considered to be joint polymers of acrylic amide and acrylic acid. They are useful in the present invention but are not so effective as polymers containing a larger proportion of amido groups.

The relative amounts of the reactants can be varied as it is not always necessary to use them in exactly equivalent amounts. However, the amount of aldehyde chosen should be such that there is not much excess, which can be detected by the odor, in the final solution.

Both organic and inorganic acids may be used to establish the desired hydrogen ion concentration in the reaction mass. Of the inorganic acids those of intermediate strength are preferable, particularly sulfuric, phosphoric, metaphosphoric, pyrophosphoric, and other polyphosphoric acids. When such acids are employed, the pH of the aqueous solution in which the reaction takes place should be adjusted to about 4. The organic acids are preferably the aliphatic caboxylic acids and may be monobasic or polybasic. They may also contain hydroxyl groups. Examples of such acids are formic, acetic, propionic, butyric, oxalic, lactic and tartaric acids. When organic acids are used, the solution in which the reaction takes place should be less strongly acid than when the inorganic acids are employed. A pH of 6 to 6.5 is desirable for the organic acids.

When an acidic medium is employed in the initial stages of the reaction, it is preferable to employ a weak acid, such as acetic acid, because the precipitate, which forms momentarily when, for example, the third ingredient is added to the reaction mixture of the other two, dissolves more readily in the presence of a weak acid. The process may also be carried out in the presence of strong acids and the products so obtained are particularly suitable for fixing tanning materials.

The order in which the reactants are mixed may be varied. For example, the amine may first be neutralized and the solution made slightly acid, after which the aldehyde is added and then the polymeric amide. If desired, the polymeric amide may be added to the amine solution followed by the aldehyde. The amine and the aldehyde may be reacted in the absence of acid and the polymeric amide added to the product. In this case the reaction product of amine and aldehyde may be acidified before the addition of the amide. The polymeric amide may be reacted with the aldehyde and the amine reacted with this product with or without the addition of acid.

The nitrogenous condensation products made according to the invention may be used, as pointed out above, for filling leather because they react not only with vegetable tans but also with those prepared from sulfite cellulose extracts, synthetic and mineral tans. Because of the fact that the new products are universal precipitants for all of these tanning agents they have many advantages over precipitants previously used, such as glue. Glue has the disadvantage when used for this purpose that, whereas it precipitates the vegetable tans, it does not precipitate all synthetic tans, unless these have been treated in some way to yield insoluble products with the glue. The precipitation of some synthetic tans by glue can be prevented by the presence of sulfite cellulose tans. This is understandable because the sulfite cellulose extracts are never precipitated by glue.

For precipitating tanning agents with the products made according to the invention, the pH of the solution may vary from 4.0 to 7.3 but is preferably adjusted to about 5.5. This range is practically the same as is used in preparing the products so that in many cases the solution in which the reactions are carried out may be employed without further treatment. When products which have been made in the absence of acid are to be used as precipitants, sufficient acid should be added before or during precipitation so as to adjust the solution to the proper pH.

The precipitates formed from the new products and tanning agents are soluble in alkaline solutions, for example in ammonia, but are reprecipitated when these solutions are acidified. When using the products to precipitate sulfite cellulose tans about equal parts by weight of the two reagents are used calculated on the dry material.

Generally speaking, the precipitants should be used at concentrations of less than 10%, preferably about 4%, for the fixation of tanning agents in leather because, if higher concentrations are used, there is danger of the leather becoming tacky.

When used as a mordant for dyeing leather, textiles, etc., the new products result in a fuller coloring and a fixation of the dye on the surface.

The new products thus have a wide field of application. They may, as has been indicated above, be used to precipitate certain materials on animal fibers. They may also be used for the same purpose on other fibrous materials, such as paper and textiles. The presence of fiber is not essential. Soluble dyes may, for example, be precipitated from their solutions thus yielding colored pigments and tanning agents or polymethacrylic amide may be precipitated in the form of an adherent mass, the adhesive properties of which may be varied or eliminated by suitable changes in its composition.

The following examples will illustrate the invention which, however, is not limited to the exact reagents and conditions of reaction given

as it may be otherwise practiced within the scope of the appended claims.

Example 1

45 parts by weight of commercial dimethylamine sulfate solution containing about 30% dimethylamine having a pH of about 4 is mixed with 20 parts by weight of 30% aqueous formaldehyde solution and the mixture heated under a reflux condenser. As soon as it begins to boil 135 parts by weight of a 10% aqueous solution of polymethacrylic amide is added in portions. In place of the polymethacrylic amide, a mixed polymer made from methacrylic amide and a small amount of methacrylic acid or acrylic acid may be used.

The resulting solution may be used to precipitate the lignin-sulfonic acid from crude sulfite liquors, for example 1000 g. of the crude liquor are treated with 94 cc. of the above solution and 400 cc. of water. The resulting precipitate is filtered and dissolved in 40 cc. of 2.5% ammonia. Any undissolved material is filtered. The clear solution may be used for filling leather. By making slightly acid the material is reprecipitated and is fixed in the leather in an insoluble condition.

The ammoniacal solution may also be used for impregnating textile, paper, artificial leather, etc.

In place of ammonia, other alkaline compounds may be used, for example, sodium hydroxide or dimethylamine.

Example 2

50 g. of 35% dimethylamine solution is mixed with 80 g. of 96% acetic acid giving a solution having a pH of about 6. To this solution 25 g. of 30% formaldehyde is added and the solution heated. To this there is added, in portions, 100 g. of a 10% aqueous solution of polymethacrylic amide. Before the addition of a further portion the precipitate which forms must be re-dissolved by boiling. The product thus obtained has a pH value of about 5.2.

The solution may be used as an assistant in dyeing; for example, chrome-tanned leather is neutralized as usual and mordanted with one per cent, of the above solution calculated on the shaved weight. It is then dyed with an acid or substantive dye. The resulting color is much fuller than without the mordant.

Example 3

125 g. of ortho-phosphoric acid (tech. conc.) is added slowly to 300 g. of 35% dimethylamine. The solution is heated and 300 cc. of 30% formaldehyde added. 1000 g. of 10% aqueous solution of polymethacrylic amide is added, in portions, to the hot solution. Before the addition of any portion the precipitate formed from the previous one must be re-dissolved by boiling. The resulting solution may be used for filling leather tanned with synthetic tans, e. g., condensation products of phenol- or cresolsulfonic acid with formaldehyde, condensation products of the sulfonic acids of naphthalene and its homologues with formaldehyde, phenol-aldehyde condensation products, condensation products of phenolsulfonic acid, urea and aldehyde, ligninsulfonic acid containing condensation products of phenol- or naphthalenesulfonic acid and formaldehyde.

Example 4

22 parts by weight of 30% aqueous formaldehyde solution is added to 45 parts by weight of dimethylamine sulfate solution containing about 30% dimethylamine. The resulting solution has a pH of about 4. This solution is boiled and 110 parts of a 10% aqueous solution of polymethacrylic amide added in portions. The resulting solution may be used for filling chrome leather. This can be carried out as follows:

The skins after the usual pickling are pretanned with 80% of water, 2% of salt, and 3% of chrome alum calculated on the weight of the skins. The skins are then drummed in a fresh bath consisting of 10% of the above solution and 20% of water. After an hour the skins are tanned in the usual way with a basic chromium tanning material. This process yields a chrome-leather with a full feel and a firm grained flank.

Example 5

45 g. of 30% formaldehyde is added to 90 g. of 35% aqueous dimethylamine solution. To this solution there is added while heating 180 g. of a 10% aqueous solution of polymethacrylic amide in portions. Before each addition the precipitate resulting from the previous addition must be dissolved by boiling. This solution is acidified by the addition of 144 cc. of 96% acetic acid and may then be used for fixing tanning materials or as an assistant in dyeing.

Example 6

0.21 part by weight of a 2.5% aqueous solution of furfurol is stirred into 5.3 parts by weight of a 3.3% aqueous solution of phenylenediaminehydrochloride. There is added while stirring one part by weight of a 10% solution of polymethacrylic amide. After heating for some time a good precipitating agent for tanning material is obtained.

The furfurol may be replaced by crotonaldehyde, acetaldehyde or allylaldehyde.

Example 7

0.5 part by weight of 85% of ortho-phosphoric acid is stirred with 5.3 parts by weight of a 3.3% aqueous solution of β-naphthylamine drochloride and the resulting mash of crystals is dissolved by heating, 0.5 part of a 2.5% aqueous solution of furfurol is added to the clear solution whilst stirring, followed by one part of a 10% solution of polymethacrylic amide. After heating for some time a product is obtained which can be used for fixing acid dyes and tanning materials containing acid groups.

Example 8

0.05 part by weight of acroleine is first stirred with 5.3 parts by weight of 3.3% aqueous solution of β-naphthylaminehydrochloride. 0.5 part by weight of 85% orthophosphoric acid and then 1 part by weight of a 10% solution polymethacrylic amide are added. After heating for some time a product is obtained which is a good precipitant for acid dyes and tanning materials containing acid groups.

This solution may be used to fix dyes on cotton, artificial silk or linen fabrics. The fabric is first treated with the solution and the dye is then applied at about 90° C. The linen may be dyed with a 0.2% solution of Diamine pure blue FF (Schulz Farbstofftabellen, vol. 1, No. 510). The artificial silk may be dyed with a 0.05% solution of Chrome Leather black RW extra (Schulz Suppl. vol. 1, page 71). The cotton may be dyed with a 0.2% solution of the diamine pure blue or with a 0.1% solution of Benzo dark green B (Schulz, vol. II, page 32, and Suppl. vol. II, page 124). The colors thus obtained are much

faster than those obtained with the same dyes on untreated fabrics.

Example 9

9.7 parts by weight of 35% glycocoll are mixed with 16.6 parts by weight of a 10% solution of polymethacrylic amide. The resulting precipitate is redissolved by heating with 4 parts by weight of 30% formaldehyde. The solution is rendered acid with 5.4 parts by weight of 96% acetic acid or with the equivalent amount of sulphuric acid, formic acid or phosphoric acid.

The product may be used for fixing tanning materials.

Example 10

2.5 parts by weight of propylamine are mixed with 1.1 parts by weight of 85% formic acid and 2.5 parts by weight of 30% formaldehyde are added. After heating, 5 parts of a 10% aqueous solution of an interpolymerization product consisting of 80 parts by weight polymethacrylic amide and 20 parts by weight methylacrylate are added successively in portions. The unsoluble residue is filtered off. The solution may be used for precipitating tanning materials from sulfite pulp.

Example 11

5 parts by weight of a 33% ethylamine are mixed with 2 parts by weight of concentrated sulphuric acid and 3.2 parts by weight of 30% formaldehyde are added to this solution while stirring. After heating 10 parts by weight of a 10% aqueous solution of an interpolymerization product consisting of 75 parts by weight polymethacrylic amide and 25 parts by weight ethylmethacrylate are added in portions and the heating continued. The product may be used for the precipitation of tanning material.

Example 12

138 parts by weight of a 42% dimethylamine are heated with 70 parts by weight of 30% formaldehyde for 2 to 3 hours under a reflux condenser until the liquid which is first cloudy has become absolutely clear. To this alkaline solution are added while stirring 2130 parts by weight of a 3.3% aqueous solution of polyacrylic nitrile which has been saponified with 65% of the amount of soda lye necessary for complete saponification, and 50 parts by weight of 30% formaldehyde.

After heating for 30 minutes the solution is rendered acid with 11 parts by weight of 96% acetic acid to pH 5.

The product may be used for fixing tanning material.

Instead of the 3.3% aqueous solution of polyacrylic nitrile there may be used a 3.3% aqueous solution of an interpolymerization product of 10 parts by weight methylmethacrylate and 90 parts by weight acrylic nitrile which has been saponified with 80% of the amount of alkali necessary for complete saponification.

Example 13

21 parts by weight of a 50% dibutylamine are mixed with 14 parts by weight of 85% orthophosphoric acid. To the solution are added 7.5 parts by weight of 30% formaldehyde. After heating, 42.5 parts by weight of a 10% aqueous solution of polymethacrylic amide is added in portions and heating is continued until the solution has become absolutely clear.

Example 14

30 parts by weight of 50% cyclohexylamine are mixed with 21 parts by weight of 96% acetic acid.

To this solution are added 7.5 parts by weight of 30% formaldehyde. After heating, 42.5 parts by weight of a 10% aqueous solution of polymethacrylic amide is added in portions while stirring and the heating is continued until the solution becomes absolutely clear.

Example 15

25.5 parts by weight of 50% piperidine are mixed with 12.5 parts by weight of 85% formic acid. To this solution 4.2 parts by weight of allylaldehyde is added. While heating and stirring, 42.5 parts by weight of a 10% aqueous solution of polymethacrylic amide is added in portions and the heating is continued until the solution becomes perfectly clear.

Example 16

32 parts by weight of 50% benzylamine and 70 parts of 10% furfurol are mixed and 10 parts of 85% formic acid is added to the solution. This solution is then heated and stirred and 42.5 parts of a 10% aqueous solution of polymethacrylic amide added, the heating being continued until the solution becomes absolutely clear.

Example 17

Chrome-tanned upper leather is neutralized and washed out as usual and then drummed for one hour with 100% of water (calculated on the shaved weight) and one per cent. of the solution prepared according to Example 2.

After this time the leather is dyed in a fresh bath with 1% Acid leather brown EG (Schultz Farbstoff-Tabellen, vol. II, page 189) and 100% of water at 65° C. After the complete absorption of the dyestuff the leather is fatliquored usually in a fresh bath. A particularly full and even dyeing is obtained.

Example 18

Chrome tanned glove-leather is neutralized, washed out and fatliquored as usual and then drummed for one hour in a fresh bath with 100% of water and 2% of the solution prepared according to Example 2.

Then the leather is dried and wet back. It is then drummed with 100% of water at 65° C. (calculated on the weight of the wet leather), 0.8% Cotton brown RVN, 0.8% Cotton brown GNJ (Schultz Farbstoff-Tabellen, vol. II, page 30, and Suppl. vol. II, page 123) and 0.5% Acid leather brown EGR (Schultz Farbstoff-Tabellen, Suppl. vol. II, page 240) until the dye solution is completely exhausted. The leather is then fatliquored, set out and dried as usual.

The treatment of the leather causes a complete absorption of the dye.

Example 19

140 g. of desized rayon staple fiber are drummed with 250 g. of the impregnation product prepared according to example 2 and 250 cc. water for 5 minutes and then pressed. It is dried at 30–40° C. and dyed with a solution containing 1 g. Acid anthracene brown RH extra (Schultz Farbstoff-Tabellen, vol. I, Nr. 134) to 1 liter water at 90° C., then washed and dried.

The resulting color is much fuller than when the impregnation product is omitted.

Example 20

500 g. of desized rayon staple fiber are drummed with 800 g. of the impregnation product prepared according to Example 2 and 800 cc. water for 5 minutes and then pressed. It is dried at 45–50° C. and dyed with a solution containing 2 g. Nigrosin WLA (Schultz Farbstoff-Tabellen, vol. I, Nr. 986 and Suppl. vol. II, page 56) to 1 liter of water at 90° C., then washed and dried.

This acid dye cannot be fixed directly on the desized rayon staple fiber but after impregnation of the fiber with the product described in Example 2, the dye can be permanently fixed.

Subject matter pertaining to the preparation of the condensation products of the polymeric amide, an amine and an aldehyde is claimed in copending application Serial No. 291,329 filed August 22, 1939. Subject matter pertaining to the use of these condensation products in the treatment of leather is claimed in copending application Serial No. 291,328, filed August 22, 1939, which on June 14, 1940, issued as U. S. Patent No. 2,205,355.

We claim:

1. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together a non-aromatic amine having at least one hydrogen atom attached to the nitrogen atom thereof, an aldehyde, and a water-soluble polymeric amide, and thereafter dyeing said material with an acid dye.

2. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together an aliphatic amine having at least one hydrogen atom attached to the nitrogen atom thereof, an aldehyde, and a water-soluble polymeric amide, and thereafter dyeing said material with an acid dye.

3. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together an aliphatic amine having at least one hydrogen atom attached to the nitrogen atom thereof, formaldehyde, and a water-soluble polymeric amide, and thereafter dyeing said material with an acid dye.

4. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together dimethylamine, formaldehyde, and a water-soluble polymeric amide, and thereafter dyeing said material with an acid dye.

5. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together dimethylamine, formaldehyde, and a water-soluble polymethacrylic amide, and thereafter dyeing said material with an acid dye.

6. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together dimethylamine, formaldehyde, and a water-soluble product containing amido groups and being obtained by the partial hydrolysis of polymeric acrylonitrile, and thereafter dyeing said material with an acid dye.

7. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together a secondary aliphatic amine having at least one hydrogen atom attached to the nitrogen atom thereof, an aldehyde, and a water-soluble polymeric amide, and thereafter dyeing said material with an acid dye.

8. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together a secondary aliphatic amine having at least one hydrogen atom attached to the nitrogen atom thereof, formaldehyde, and a water-soluble polymeric amide, and thereafter dyeing said material with an acid dye.

9. The process of dyeing organic fibrous material which comprises treating said material with a product capable of forming an insoluble compound with an acid dye and which is prepared by condensing together a secondary aliphatic amine having at least one hydrogen atom attached to the nitrogen atom thereof, furfurol, and a water-soluble polymeric amide, and thereafter dyeing said material with an acid dye.

10. The process of dyeing organic fibrous material which comprises treating said material with an acid dye and a product capable of forming an insoluble compound with said dye and which is prepared by condensing together a non-aromatic amine having at least one hydrogen atom attached to the nitrogen atom thereof, an aldehyde, and a water-soluble polymeric amide.

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