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FUGITIVE TINTING OF TEXTILE MATERIALS

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This invention relates to textile tinting compositions and to the fugitive tinting of textile materials, especially the fugitive tinting of fibres of cellulose acetate or other cellulose ester or ether.

It is a common practice in the textile industry to apply fugitive tints to textile threads and other textile materials in order to assist identification during processing. It is often a great advantage to be able to identify particular ends in a warp during weaving or to distinguish at a glance one kind of yarn from another. Again, in preparing mixtures of two different kinds of staple fibre, for example a mixture of cellulose acetate staple fibre and wool fibres, it is convenient to tint one of the fibres so that a visual examination of the mixture enables one to tell whether the blending of the fibres is complete or adequate. It is of course essential that the fugitive tint applied should be readily removable, preferably by a normal scouring operation, when it has served its purpose. For this to be possible in the generality of cases, the tint must be such as to resist fixation on the textile fibre to which it has been applied, or on any associated textile fibres, as a result of such treatments as the material may have undergone, for example sizing, steaming, conditioning with respect to moisture content, crabbing, or dry heat setting treatments such as are sometimes applied to fabrics of oriented fibres of synthetic linear polymers, e. g. nylon 66. Crabbing is a pre-setting treatment often applied to fabrics consisting of or containing wool as the first wet treatment of the fabric after leaving the loom. As ordinarily practised it involves a treatment with plain water at or near the boil.

It is very difficult to find tints which are fugitive following the various treatments which a mixture of wool fibres and cellulose acetate fibres may undergo in the ordinary textile processing involved in converting the mixture into a yarn and the yarn into a fabric. Acid wool dyes are often satisfactory but we have observed that they sometimes become fixed by a steam treatment or even by treatment with limited quantities of water in the cold. Fixation has occasionally occurred for instance when cops of yarn composed of wool fibres and cellulose acetate staple fibres have been conditioned by leaving them for several hours in a closed room on a wet porous brick floor. Cold water tests of comparable severity which can be carried out in the laboratory are as follows: (1) For yarn or loose fibre a ½ inch test tube six inches long is firmly packed full of the tinted material and inverted in a 100 ml. beaker containing 4 ml. of water and left overnight. (2) For fabrics a piece of the tinted fabric is laid on a glass plate and on it is placed, circular end downwards, a stainless steel cylinder ¾ inch diameter and ¾ inch long having a ¼ inch hole bored through axially; 0.5 ml. water is dropped into the hole and the assembly left overnight. In each case the material is then dried and tested for ease of removal of the tint by a short soaping. When tested in this way many acid dyes become fixed

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on wool fibres or cellulose acetate fibres so that they cannot be removed by a simple scouring in soap solution. Acid dyes moreover are liable to become fixed on cellulose acetate fibres containing a substantial proportion of acetone, say 7 to 10%. Fixation is therefore quite likely if a solution of an acid dye is applied to cellulose acetate filaments immediately after their formation by dry spinning from an acetone solution of cellulose acetate.

We have now found that textile fibres can be tinted very satisfactorily by means of a direct cotton dyestuff in association with a water-soluble addition polymer of an N-vinyl lactam and particularly an addition polymer of N-vinyl pyrrolidone. For example, cellulose acetate staple fibre may be tinted by moistening it with water containing 1 g. per litre of Chlorazol Fast Pink BKS and 4 g. per litre of commercial polyvinyl pyrrolidone as sold under the trade name Albigen A and then dried. The weight of water may be 50 to 100% based on the weight of the fibre. The tinted fibre so produced may be mixed with wool, or with regenerated cellulose staple fibre, the mixture spun into a yarn and the latter woven into a fabric; the tint is readily removed by a mild soap scour even though the material has been left wet for several hours, as in the above cold water test, or steamed for 15 minutes at 220° F. A further advantage resulting from the presence of the polymerised N-vinyl lactam is the very good colour value obtainable from the direct cotton dye. Normally, if cellulose acetate fibres are moistened with a simple aqueous solution of a direct cotton dye and thereafter dried, very little colour is apparent. It appears that something of the nature of a spreading agent is necessary in order to prevent agglomeration of the dye into relatively large particles when the aqueous solution thereof is dried on the fibres; the addition polymer of an N-vinyl-lactam serves this purpose.

The product Albigen A referred to above is an aqueous solution containing approximately 30% by weight of polyvinyl pyrrolidone; when the solid matter content is adjusted to 30% by weight the resulting aqueous solution has at 20° C. a viscosity of 62 seconds, taking the viscosity of glycerol as 100 seconds under the same conditions.

The preferred water-soluble addition polymer employed is the homopolymer of N-vinyl pyrrolidone referred to above. Pyrrolidone is of course the lactam of gamma-aminobutyric acid. Homopolymers of vinyl derivatives of lactams of other amino fatty acids may be employed for example, N-vinyl-2-piperidone and N-vinyl caprolactam. Again, water-soluble heteropolymers derived from two or more N-vinyl lactams as the polymerisable constituents may be employed, likewise water-soluble heteropolymers derived from both an N-vinyl lactam and another ethylenic compound capable of polymerising therewith, for example, a neutral polymerisable ethylenic compound such as acrylonitrile, vinyl chloride, an acrylic ester or a methacrylic ester.

The proportion of polymerised vinyl lactam necessary to prevent fixation of the cotton dye can very easily be determined by experiment. When using commercial direct cotton dyes and the commercial polyvinyl pyrrolidone product sold as Albigen A, very satisfactory results are in general obtained when the weight of polymer product employed is from 3 to 6 times the weight of the dyestuff. If the commercial direct cotton dye contains 20% of actual dye (a usual proportion in the case of ordinary "single strength" direct cotton dyes) and the commercial polyvinyl pyrrolidone (Albigen A) contains 30% of actual polyvinyl pyrrolidone (as is approximately the case), the figures given above correspond with from 4.5 to 9 parts by weight of actual polyvinyl pyrrolidone to each part by weight of actual dye. Higher proportions of polymer may be employed but without any substantial

gain. Generally speaking very good results are obtained with about 6 parts of actual polyvinyl pyrrolidone to each part of actual dye.

Various direct cotton dyes may be used when tinting textile fibres in accordance with the invention. In general it is advantageous to use direct cotton dyes having a comparatively long time of half-dyeing (T. H. D.) on viscose rayon as measured in the manner described in "Dyeing with Coal-Tar Dyestuffs" C. M. Whittaker and C. Wilcock, 5th edition, page 239. Thus the dyes may have a time of half-dyeing of at least 10 minutes, for example at least 50 minutes. Examples of direct cotton dyes which have been found to give excellent results are the Chlorazol Fast Pink BKS (I. C. I.) (Colour Index No. 353) referred to above (T. H. D.=280 minutes), Chlorantine Fast Blue 3GLL (Ciba) (T. H. D.=126 minutes), and Diphenyl Fast Blue-Green BL (Solophenyl Blue Green BL) (Geigy) (T. H. D.=200 minutes). On the other hand very good results have been obtained with Chrysophenine G (Colour Index No. 365) which has a time of half dyeing of only 2.26 minutes. Other direct cotton dyes which may be used are Solar Green 5G (Sandoz), Chlorantine Fast Green BLL (Ciba), Durazol Blue 2RS (I. C. I.), Durazol Fast Paper Blue 10 GS (I. C. I.), Durazol Fast Rubine B (I. C. I.), Diphenyl Fast Brilliant Pink BL (Geigy), and Sun Yellow 3G.

The dye and addition polymer of an N-vinyl lactam may be present on the fibres in association with textile dressing agents, for example sizes or lubricants.

The direct cotton dye and polymer of an N-vinyl lactam are conveniently applied to the textile fibres as an aqueous solution, following which the fibres may be dried to leave thereon a deposit of dye and polymer. The solution may contain a dressing agent for the textile fibres, for example a sizing agent or a lubricant. A lubricant, e. g. a mineral oil, may for example be emulsified in the solution by means of a suitable emulsifying agent.

Various ways of applying the solutions may be employed. Thus cellulose acetate fibre may be sprayed with sufficient of an aqueous solution of the direct cotton dye and polymerised vinyl lactam to yield the desired depth of tint and thereafter dried. Again the staple fibre may be saturated with the tinting liquid and thereafter squeezed or hydro-extracted to leave the requisite proportion of liquid on the material. For simultaneous tinting and lubrication of cellulose acetate staple fibre the latter may be soaked in a 0.1 to 1 g. per litre aqueous solution of Chlorazol Fast Pink BKS (or other of the direct cotton dyes specified above) containing 3 to 5 g. per litre of Albigen A and having 0.1 to 1% of mineral oil (viscosity 50 seconds Saybolt at 100° F.) emulsified therein by means of the triethanolamine salt of oleyl sulphate. The material is then hydro-extracted so as to leave therein from 30 to 80% of liquid (based on the dry weight of the material) and is thereafter dried.

If desired the aqueous dye solutions containing water-soluble addition polymers of N-vinyl lactams may be applied to cellulose acetate filaments continuously with their production by dry spinning methods. For example, cellulose acetate filaments may be dry-spun from a number of spinning nozzles, lubricated by contact with a wick fed with mineral oil containing an antistatic agent, and gathered together to form a tow. The dye solution is applied to the tow, for example by spraying or by merely allowing it to trickle on to the tow. The tow may then be collected in cans for further treatment. Alternatively it may be forwarded directly to a crimping device of the kind in which the tow is forced by means of feed rolls into a box with a loaded exit door through which the crimped tow emerges; in this case the water of the aqueous tinting fluid may serve to assist the crimping operation. The tow may then pass directly to a suitable cutting machine for converting it into staple fibre.

The new method of fugitive tinting is particularly valuable for cellulose acetate fibres whether in the form of

staple fibres or continuous filaments. It is, however, of especial utility for cellulose acetate staple fibres for the reasons given above, namely that the tinted staple fibres may be mixed with wool and the mixture readily worked up into yarns or fabrics from which the tint is easily and completely removed by a mild scouring operation.

The new tinting process may also be applied to fibres of other cellulose esters or fibres of cellulose ethers, for example to fibres of cellulose propionate, acetate-propionate or acetate-butyrate, or to fibres of ethyl-cellulose. Again the tinting process may be applied to textile fibres of other kinds for example to animal fibres, e. g. wool or silk, or to cellulose fibres for example cotton or fibres of regenerated cellulose such as those produced by the viscose process. Further, it may be applied to fibres of synthetic condensation or addition polymers. Thus it may be applied to fibres of linear polyamides, for example linear polyamides from dicarboxylic acids and diamines, e. g. nylon 66, fibres of linear polyaminocarboxylic acids, e. g. poly-aminocaproic acid, fibres of polyurethanes, fibres of linear polyesters, e. g. the polyester from glycol and terephthalic acid, and to fibres of the following condensation polymers: acrylonitrile polymers, e. g. polyacrylonitrile and acrylonitrile/vinylchloride co-polymers, vinyl chloride/vinyl acetate copolymers, and vinylidene chloride/vinyl chloride copolymers. Fabric of nylon 66 yarns tinted in accordance with the invention with Chlorazol Fast Pink BKS and polyvinyl pyrrolidone may for instance be heat set dry at 225° to 230° C. without rendering the tint proof against removal by scouring for 30 minutes in 2 grams per litre soap solution containing 0.3 gram per litre of soda ash.

The method is valuable even when the fibre to be tinted is not one which is liable to become permanently stained when conventional tinting methods are employed, as in the case of polyglycolterephthalate; the use of the new method ensures that any more sensitive fibres processed in association with the tinted fibre do not become permanently stained by dye transferred from the tinted fibre.

The invention includes concentrated preparations comprising the direct cotton dye and the water-soluble addition polymer of an N-vinyl lactam and which can, by mixing with water, be converted into tinting liquids suitable for the tinting of textile fibres as described above. Such concentrated preparations may contain from 1% of actual dye and upwards, for example from 2% to 10% or 15% or more, the dye being in association with the requisite proportion of the N-vinyl lactam polymer, e. g. with from 4.5 to 9 times its weight of polyvinyl pyrrolidone. These concentrated preparations may be in the form of aqueous liquids or pastes or in the form of solids, powders or otherwise, which latter may be substantially water-free. The preparations may contain materials other than the dye and polymerised N-vinyl lactam, for example textile lubricants or other textile dressing agents, or dextrin, inorganic salts, or other substances such as are commonly present in commercial direct cotton dyes.

Concentrated preparations are easily prepared by mixing commercial direct cotton dyes with a concentrated aqueous solution of the polymerised N-vinyl lactam, whereby clear solutions can be obtained. Substantially water-free preparations can be obtained by drying. For instance by stirring 1 part by weight of dry Chlorazol Fast Pink BK 200% with 8 parts by weight of Albigen A (30% solids) a clear ruby-red solution is obtained which contains about 4.5% of actual dye and can be diluted with water to form tinting fluids for use in accordance with the invention. By drying in thin layers this ruby-red solution can be converted into a friable film which is readily broken up into a powder containing about 12% of dye. Alternatively the solution may be spray-dried in order to obtain a dry powder directly. The film or powder is very readily soluble in cold water.

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Similar compositions may be prepared by replacing the Chlorazol Fast Pink BK with other of the direct cotton dyes referred to above.

As already indicated textile fibres tinted in accordance with the invention can very easily be freed from the tint by simple treatments. However where the tinted fibres are of cellulose or in association with cellulose fibres it is inadvisable to subject the material, in the presence of the tint, to treatments with aqueous liquids containing substantial proportions of electrolyte. Otherwise there is, in the case of certain dyes, some risk of fixation of dye on the cellulose. If therefore the normal processing of the material calls for such a treatment it is advisable first to remove the tint by treatment with an aqueous liquid which does not contain any substantial proportion of electrolyte; this treatment may be effected at a low liquor to goods ratio, e. g. less than 10:1.

Having described our invention what we desire to secure by Letters Patent is:

1. Fugitively tinted textile materials, wherein the tint comprises a dry composition of a direct cotton dye in association with a water-soluble addition polymer of an N-vinyl lactam wherein said composition is present on the fibers of said textile materials as a surface deposit.

2. Fugitively tinted textile materials, wherein the tint comprises a dry composition of a direct cotton dye in association with a water soluble homo-addition polymer of an N-vinyl lactam wherein said composition is present on the fibers of said textile materials as a surface deposit.

3. Fugitively tinted textile materials, wherein the tint comprises a dry composition of a direct cotton dye in association with polyvinyl pyrrolidone wherein said composition is present on the fibers of said textile materials as a surface deposit.

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4. Fugitively tinted textile materials according to claim 3, wherein the proportion of polyvinyl pyrrolidone is from 4.5 to 9 times the weight of actual dye present.

5. Fugitively tinted textile materials of cellulose acetate, wherein the tint comprises a direct cotton dye in association with a water-soluble homo addition polymer of an N-vinyl lactam.

6. Fugitively tinted textile materials of cellulose acetate, wherein the tint comprises a direct cotton dye in association with polyvinyl pyrrolidone.

7. Fugitively tinted cellulose acetate textile materials according to claim 6, wherein the proportion of polyvinyl pyrrolidone is from 4.5 to 9 times the weight of actual dye present.

8. Fugitively tinted cellulose acetate textile materials according to claim 5, wherein the direct cotton dye has a time of half-dyeing of at least 10 minutes.

9. A method of imparting a fugitive tint to textile materials of cellulose acetate which comprises impregnating the materials with an aqueous solution containing a direct cotton dye and polyvinyl pyrrolidone and thereafter drying the materials.

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