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2,802,714

FUGITIVE TINTING WITH DIRECT DYES AND ACRYLAMIDE POLYMERS

Henry Charles Olpin, Alexander James Wesson, and Alexander McGill, Spondon, near Derby, England, assignors to British Celanese Limited, a corporation of Great Britain

Application November 30, 1953, Serial No. 395,323

Claims priority, application Great Britain
December 10, 1952

10 Claims. (Cl. 8—56)

This invention relates to the fugitive tinting of textile materials and especially to the fugitive tinting of fibers 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 fibres, as a result of such treatments as the material may have undergone, for example sizing, steaming, conditioning with respect to moisture content, or heat setting treatments such as are commonly applied to fabrics or oriented fibres of synthetic linear polymers, e. g. nylon 66.

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 over night. (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 over night. 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 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

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their formation by dry spinning from an acetone solution of cellulose acetate.

According to our U. S. application S. No. 377,957 filed September 1, 1953, 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 a polymer from N-vinyl-2-pyrrolidone. Poly-N-vinyl-2-pyrrolidone is sold under the trade name Albigen A. The direct cotton dyestuffs form complexes with these poly-N-vinyl lactams which enable fibres such as cellulose acetate, wool, cotton, rayon and other fibres to be tinted with a solution of the complexes and which enable the tints when they have served their purpose to be removed very readily by a mild soap scour. As indicated the preferred polymer according to the prior specification is poly-N-vinyl pyrrolidone. Other polymers which may be used according to the said specifications are poly-N-vinyl-2-piperidone and poly-N-vinyl-epsilon-caprolactam.

The polymer of an N-vinyl lactam is effective because it has a very high affinity for the dyestuff which in consequence remains as the complex with the polymer instead of entering and colouring the textile fibre. This holds also during subsequent removal of the tint by an aqueous treatment, the dye and polymer being removed together and the fibre left substantially unstained. The principle involved is that the dye is applied to the fibre in conjunction with a polymer which has a higher affinity for the dye than has the fibre. We have found indeed that this principle is of general application in the fugitive tinting of textile fibres and according to our invention we tint textile fibres with a dyestuff in conjunction with a polymer, soluble in aqueous liquids, which has a higher affinity for the dye than has the fibre.

Preferably the polymer is one which is soluble in water alone but may be one which is insoluble in water alone but soluble in water containing an acid or alkaline substance, i. e. a substance yielding hydrogen ions or a substance yielding hydroxyl ions in water. Thus it may be one soluble in an aqueous liquid at some pH value between 2 and 12 and particularly between 4 and 10.

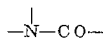
The polymer may be one which has good affinity for and can be used in association with or in the form of a complex with a direct cotton dyestuff or one which has good affinity for and can be used in association with or in the form of a complex with an acid wool dye. Again the polymer can be one which can be used with either a direct cotton dye or an acid wool dye. The polymers used according to the present invention are preferably water-soluble, as already indicated, or soluble or at least readily emulsifiable in a dilute aqueous soap solution. They may be such as can be synthesised by addition polymerisation or such as can be synthesised by condensation polymerisation. Further in all cases they are of high molecular weight and preferably sufficiently high molecular weight to be fibre forming; for example they may have molecular weights, calculated from their viscosity, of the order of 3-4000 or more and preferably over 6000. In all cases they contain nitrogen atoms and preferably the nitrogen atoms are present in the polymer molecule as tertiary nitrogen atoms i. e. they do not carry hydrogen atoms attached to nitrogen. Further, in most cases we prefer to use non-crystallisable polymers and also we prefer to use polymers the molecules of which do not lend themselves readily to hydrogen bonding one with another. In most cases absence of hydrogen bonding is due to absence of hydrogen attached to nitrogen but, in some cases, due to the position of an NH group in the polymer, hydrogen bonding is difficult or impossible. Thus, for example, in the condensation polymer obtained from C. C. tri(beta-carboxyethyl)-monomethylamine and a di-secondary amine, an amino-

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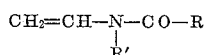
alcohol in which the amine group is secondary, or a glycol, notwithstanding the fact that such a polymer contains a lactam ring in which the nitrogen carries a hydrogen atom, nevertheless the polymer does not appear to be hydrogen bonding and is not crystallisable. This is presumably because of the position of the lactam ring in the polymer molecule.

Particularly useful polymers for use in conjunction with direct cotton dyes are water-soluble polymers containing recurrent nitrogen atoms each directly attached to a $-\text{CO}-$ group.

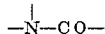
Vinyl type addition polymers which are useful in association with or as complexes with direct dyestuffs include the polymers from N-vinyl carboxylic acid amides, preferably amides in which the nitrogen atom is tertiary. The addition polymers may be homopolymers but are preferably co-polymers made by co-polymerising the nitrogenous monomer with a vinyl compound of very hydrophile character or which can be converted after the polymerisation to a hydrophile component, whereby products of improved solubility in water may be obtained. Thus the nitrogenous monomer may be co-polymerised with acrylamide or it may be co-polymerised with a vinyl ester which may in the polymer be converted into the corresponding hydroxyl compound by saponification. Again it may be copolymerised with a polymerisable carboxylic acid, e. g. acrylic acid or methacrylic acid, or with saponifiable derivatives thereof such as esters, which may be converted to the free acid or salt, or with maleic anhydride which again may be converted in the polymer to the free acid or salt. The carboxylic amide may be an open chain carboxylic amide by which we mean that the



group thereof is not part of a ring; in this case the general formula of the monomers of such polymers may be written



Such polymers are allied in structure to the poly-N-vinyl lactams of our prior application and have similar properties. The radicals R and R' may be hydrogen alkyl, aralkyl or aryl and may be bulky radicals so as to inhibit crystallisation. One or both of them may for example be isopropyl, isobutyl or tertiary butyl. Examples of such polymers are the polymers of N-vinyl-N-methylacetamide, N-vinyl-N-isopropylacetamide, N-vinyl-N-isobutylacetamide, N-vinyl-N-tert-butylacetamide, N-vinyl-N-methyl-n-butyramide and N-vinyl-N-isobutylacetamide, or the copolymers of any of these monomers with acrylamide or methacrylamide, e. g. a co-polymer of N-vinyl-N-isopropylacetamide or N-vinyl-N-tert-butylacetamide with acrylamide in about equimolecular proportions. Again, the polymer may be one of a vinyl derivative of a heterocyclic compound containing only carbon and nitrogen in the ring and in which each ring nitrogen atom is united directly to a ring carbon atom which is linked to oxygen by a double bond. Thus the polymer may be one of an N-vinyl-cyclic carboxylic amide by which we mean that the

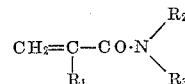


group forms part of a ring. Polymers of this category are: polymers of N-vinyl phthalimide and N-vinyl succinimide and their substitution products; N-vinyl-N'-alkyl, aralkyl or aryl hydantoins; and N-vinyl-N'-alkyl, aralkyl or aryl lactimides, for example 1-vinyl-4-methyl- or ethyl-2,5-diketopiperazine; copolymers of any of these monomers with acrylamide or methacrylamide, for example a co-polymer of N-vinyl succinimide or 1-vinyl-4-methyl-2,5-diketopiperazine with acrylamide in about equimolecular proportions. Generally the monomers for such

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polymers may be produced by reacting acetylene with the appropriate secondary acid amide, for example methyl acetamide, isopropyl acetamide, methyl-n-butyramide, phthalimide, succinimide, an N-alkyl hydantoin or 4-alkyl-2,5-diketopiperazine.

A further series of addition polymers, again of closely similar properties comprises the addition polymers of the amides, particularly the tertiary amides, of acrylic acid, methacrylic acid and the like. The monomers for the production of such polymers may have the formula



Where R₁ is hydrogen or a methyl or other alkyl group and R₂ and R₃ are hydrogen, alkyl or aryl groups. If desired R₂ and R₃ may together or together with a further atom, e. g. an oxygen atom, form a divalent radical so as to form a ring as for example in the pyrrolidide, piperidide or morpholide of acrylic or methacrylic acid. If R₂ and R₃ are separate radicals it is advantageous that at least one of them should be bulky as explained above with reference to the N-vinyl carboxylic amides. Examples of such polymers are those of acrylic acid amide, dimethylamide, di-isopropylamide, tert-butylamide, or methyl-benzylamide, of methacrylic acid amide, dimethylamide, di-isopropylamide, benzylamide, and methyl-benzylamide, and of acrylic acid or methacrylic acid, pyrrolidide, piperidide, or morpholide.

A further series of polymers, which can be used in association or as complexes with direct cotton dyestuffs, may be made by condensation polymerisation and may be water-soluble polyamides or polyester amides containing lactam or lactimide rings in which preferably all the nitrogen atoms are tertiary or are so placed in the polymer molecule that they cannot form hydrogen bonds. Examples of such condensation polymers include the condensation product from C. C. C-tri(beta-carboxyethyl)-mono-methylamine and diethylene glycol, dipropylene glycol, or a polyethylene glycol or a polypropylene glycol, or from the same acid and di-(beta-methylamino)-diethyl ether. The preparation of the mono-amino-tricarboxylic acid referred to above is described in U. S. Patent No. 2,502,548. This type of amino-carboxylic acid has the advantage that the lactam ring which is formed is so placed with respect to the polymer molecule that hydrogen bonding and crystallisation are substantially impossible. Further, it will be noted that the three carboxy groups are symmetrically disposed with reference to the carbon atom attached to the amino group so that no complications ensue due to different isomers being formed by condensation of different carboxy groups with the various functional groups of the bifunctional reagent with which the amino-tricarboxylic acid is to be condensed and any one of the carboxy groups can form the lactam. This amino-tricarboxylic acid may be used in the free state or as a simple ester, for example the trimethyl or triethyl ester, as the lactam or as a simple diester of the lactam. A further condensation polymer which is included in the present category of polymers is that obtained from 2,5-diketopiperazine-1,4-diacetic acid and diethylene glycol, dipropylene glycol, or a polyethylene glycol or a polypropylene glycol, or from some acid and di-(beta-methylamino)-diethyl ether. The diketopiperazine-diacetic acid may be prepared by self-condensation of imino-diacetic acid or its esters and may be used as such or in the form of a diester, e. g. a dimethyl or diethyl ester.

A further series of condensation polymers which may be employed together with cotton dyestuffs according to the present invention comprises the water-soluble polyurethanes obtainable by condensing di-chloroformic esters of polyglycols with diamines, e. g. the product from the di-chloroformic ester of a polyethylene glycol containing on the average 2 to 4 ether oxygen atoms per molecule

with hexamethylene diamine or N:N'-dimethyl-hexamethylene diamine.

Again in the case of using for the present invention polymers which have an affinity for wool dyestuffs, the polymers may be either of the addition type or the condensation type. In all cases they contain basic nitrogen and in most cases the basic nitrogen is in the form of tertiary nitrogen atoms. Among the addition polymers which may be included in the compositions of the present invention are the polymers obtainable from vinyl pyridines for example, 2-vinyl pyridine or 5-vinyl-2-methyl pyridine and the vinyl N-alkyl, aralkyl or aryl pyrrols, e. g. 1-vinyl-pyrrole, and the 1-alkyl-2-vinyl pyrrols, e. g. 1-methyl-2-vinyl pyrrole. Usually the monomers for such polymers may be produced by dehydrogenation of the corresponding compound containing an ethyl group instead of a vinyl group or dehydration of the corresponding hydroxyethyl compound. Further basic polymers for the production of such polymers are the 1-alkyl-3-vinyl-2-imidazolidones, the 1-alkyl-2-vinyl-3-pyrazolidones and the 1-vinyl-5-pyrazolones, e. g. 1-vinyl-5-pyrazolone and 1-vinyl-3-methyl-5-pyrazolones. The basic monomers are preferably co-polymerised with vinyl compounds of more hydrophilic character or which can be converted after polymerisation into a hydrophilic component. Such hydrophilic components are N-vinylpyrrolidone, acrylamide, methacrylamide and their N-alkyl derivatives, acrylic acid, and methacrylic acid. Again vinyl esters e. g. vinyl acetate, may be used, and the co-polymers saponified, or maleic anhydride or an ester thereof may be used and the co-polymer saponified to yield the free acid. Suitable polymers may be made for instance by copolymerising one of the above basic monomers, e. g. 2-vinyl pyridine, with N-vinyl pyrrolidone, or by co-polymerising with vinyl acetate and saponifying; the molar proportion of the basic monomer may be from 30 to 70%.

It will be seen that generally for use with cotton dyestuffs we use polymers containing acid amide groups and preferably acid amide groups in which the nitrogen atoms are either tertiary or if secondary are so placed that they cannot hydrogen bond and for acid dyestuffs we use polymers containing basic nitrogen atoms and preferably tertiary nitrogen atoms or nitrogen atoms which when not tertiary are so placed that they cannot hydrogen bond.

The addition polymers may be made by the usual methods of addition polymerisation using for example per compounds, for example persulphates, as catalysts, and may be carried out either in aqueous solution or in aqueous emulsion, the latter particularly for copolymers which have to be converted by hydrolysis or otherwise into water-soluble polymers subsequent to the polymerisation.

The proportion of polymer necessary to prevent fixation of the cotton or wool dyestuffs can very easily be determined by experiment. Satisfactory results are generally obtained with 0.5 to 2 or 3 parts by weight of polymer to each part by weight of the commercial dyestuff. If, as is usual, the commercial acid wool dyestuff or cotton dyestuff contains 20% of actual dye then this proportion corresponds with a proportion 2.5 to 10 or 15 parts by weight of polymer to 1 part of actual dyestuff. Generally speaking, very good results are obtained with only about 6 parts of the polymer to each part of dyestuff.

In the case of using direct cotton dyes in accordance with the invention the dye may be any of those mentioned in our earlier application referred to above. In the case of using acid wool dyes the dye is preferably one which contains at least two sulphonic acid groups. Examples of such dyes are Tartrazine (Colour Index No. 640), Amarant (Colour Index No. 183), and Indigo Carmine (Colour Index No. 1180).

The cotton or wool dyestuff and the polymer or the complex formed therefrom may be 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 fibre, 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 dye and polymer 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.

If desired the aqueous dye solutions containing the water-soluble polymers 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 anti-static agent, and gathered together to form a tow. The dye-polymer solution is applied to the tow, for example by spraying or by merely allowing it 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 or other fibres and the mixture 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 addition polymers: acrylonitrile polymers, e. g. polyacrylonitrile, acrylonitrile/vinylchloride copolymers, acrylonitrile/vinylidene chloride co-polymer, vinyl chloride/vinyl acetate copolymers, and vinylidene chloride/vinyl chloride copolymers.

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 or acid wool dye and the water-soluble polymer 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 pure dye and upwards, for example from 2% to 10%, the dye being in association with the requisite proportion of the polymer.

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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 polymer, for example textile lubricants or other textile dressing agents.

Concentrated preparations are easily prepared by mixing commercial direct cotton or acid wool dyes with a concentrated aqueous solution of the appropriate polymer, whereby clear solutions can be obtained. Substantially water-free preparations can be obtained by drying. The concentrated preparations can be diluted with water to form tinting fluids suitable for use in accordance with the new invention.

The invention is illustrated by the following examples:

Example 1

One part of Chlorazol Fast Pink BKS (I. C. I.) (Colour Index No. 353) and 1.5 parts of polyacrylamide are dissolved in 5000 parts of water. Cellulose acetate staple fibre is immersed in the resulting solution and then squeezed or hydroextracted so that the staple fibre retains about 50% of its weight of liquid based on the dry weight of the fibre. It is then dried. The material is tinted a pink shade and the tint is very readily removed by a mild soap scour. The tinted fibre can be mixed with wool fabrics from which the tint is likewise readily removed by a mild scour.

Similar results may be obtained by replacing the polyacrylamide by poly-acrylpyrrolidide or by a co-polymer of N-vinyl-N-tert-butyl-acetamide with acrylamide in approximately equimolecular proportions. Likewise the Chlorazol Fast Pink BKS may be replaced by another of the direct cotton dyes referred to in our earlier application mentioned above.

Example 2

One part of Chlorazol Fast Pink BK 200% is mixed with a concentrated aqueous solution of 3 parts of polyacrylamide and heated to effect solution. The resulting coloured solution is then dried in thin layers and the resulting film broken up into a powder. The product contains about 10% of actual dye and can be used directly for the preparation of textile tinting liquids.

The polyacrylamide may be replaced by an equal weight of polyacrylpyrrolidide.

Example 3

A co-polymer is prepared from approximately equimolecular proportions of 2-vinyl pyridine and vinyl acetate and is saponified. 3 parts of the saponified product and one part of Indigo Carmine XS (I. C. I.) (Colour Index No. 1180) are made to about 5000 parts with water and the resulting coloured solution is used to tint cellulose acetate fibre as described in Example 1. The tinted fibre is readily cleared of tint by a mild soap scour. The dye specified may be replaced by other of the acid wool dyes referred to above.

This application is a continuation-in-part of our U. S. application Serial No. 377,957 filed September 1, 1953.

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

1. Fugitively tinted textile materials, wherein the tinting agent carried by the textile material comprises a mixture

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of a direct cotton dye with a water-soluble addition polymer of a compound selected from the group consisting of acrylic acid amide and methacrylic acid amide and their N-alkyl derivatives, said polymer having a molecular weight of at least 3000 and being present in the proportion of from 2.5 to 15 parts by weight to each part by weight of actual dyestuff.

2. Fugitively tinted textile materials, according to claim 1, wherein the polymer is a water-soluble addition polymer of acrylamide.

3. Fugitively tinted textile materials, according to claim 1, wherein the polymer is polyacrylamide.

4. Fugitively tinted textile materials of cellulose acetate, wherein the tinting agent carried by the textile material comprises a mixture of a direct cotton dye with a water-soluble addition polymer of a compound selected from the group consisting of acrylic acid amide and methacrylic acid amide and their N-alkyl derivatives, said polymer having a molecular weight of at least 3000 and being present in the proportion of from 2.5 to 15 parts by weight to each part by weight of actual dyestuff.

5. Fugitively tinted textile materials of cellulose acetate, according to claim 4, wherein the polymer is polyacrylamide.

6. A method of imparting a fugitive tint to textile materials which comprises drying the materials after impregnating them with an aqueous solution containing a direct cotton dye and a water-soluble addition polymer of a compound selected from the group consisting of acrylic acid amide and methacrylic acid amide and their N-alkyl derivatives, said polymer having a molecular weight of at least 3000 and being present in the proportion of from 2.5 to 15 parts by weight to each part by weight of actual dyestuff.

7. A method of imparting a fugitive tint to textile materials, according to claim 6, wherein the textile materials are of cellulose acetate and in which the polymer is polyacrylamide.

8. A tinting composition for the fugitive tinting of textile materials, said composition comprising in admixture a direct cotton dye and a water-soluble addition polymer of a compound selected from the group consisting of acrylic acid amide and methacrylic acid amide and their N-alkyl derivatives, said polymer having a molecular weight of at least 3000 and being present in the proportion of from 2.5 to 15 parts by weight to each part by weight of actual dyestuff.

9. A tinting composition for the fugitive tinting of textile materials, according to claim 8, wherein the polymer is a water-soluble addition polymer of acrylamide.

10. A tinting composition for the fugitive tinting of textile materials, according to claim 8, wherein the polymer is polyacrylamide.

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