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INHIBITION OF ACID-FADING ON DYED CELLULOSE ACETATE WITH N:N' DIPHENYLETHYLENE DIAMINE

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The present invention relates to a process for treating materials consisting of or containing cellulose esters or ethers in order to enhance the fastness of the colourations on the aforesaid materials when they are dyed or otherwise coloured by the application of dyestuffs thereto.

It is known that materials consisting of or containing cellulose esters or ethers which have been coloured by dyeing or printing tend to fade when exposed to the action of the products of combustion of coal gas, that is to say, when they are kept in an atmosphere which is contaminated with fumes from burning coal gas. For example, if cellulose acetate artificial silk which has been dyed is stored in a warehouse in which coal gas is consumed for lighting or other purposes, the colour of it is liable to fade. This fault is the more troublesome because it is those parts of the cellulose acetate artificial silk which are most directly exposed to the fumes from the burning gas, e. g.. the edges of a roll of the acetate artificial silk cloth, which are worst discoloured. As a result the material becomes disfigured. It consequently depreciates in value and may even prove unsaleable. Whilst the effect just referred to is common to various classes of dyestuff, it is particularly prevalent in respect of anthraquinone dyestuffs. Especially is this the case with those yielding violet, blue or green shades. By way of example we mention the dyestuffs 1-amino-4-methylaminoanthraquinone (violet shade), 1:4:5:8-tetraaminoanthraquinone (blue shade) and 1(p-aminoanilino) - 4-acetylmethylaminoanthraquinone (green shade): We have now found that this effect occasioned by the action of fumes from burning coal gas can be advantageously hindered or prevented by applying to the materials consisting of or containing cellulose esters or ethers an N-substituted diamine as defined below.

Accordingly the present invention relates to a process for treating materials consisting of or containing cellulose esters or ethers comprising applying thereto an N-substituted diamine of the general formula $RR'N-(CH_2)_n-NRR'$, wherein R represents hydrogen, methyl, ethyl or hydroxyethyl; R' represents phenyl which may carry simple substituents such as alkoxy, alkyl or halogen, and n stands for 2–6.

By way of N-substituted diamines there may be used according to the present invention, for example, N:N'-dimethyl-N:N'-diphenylethylene diamine, N:N' - diethyl - N:N'-diphenylethylene diamine, N:N'- dimethyl-N:N'- diphenyltrimethylene diamine, N:N'-diethyl-N:N'-diphenyltrimethlyene diamine (respecting the preparation of the foregoing compounds, see Fröhlich, Berichte der deutschen Chemischen Gesellschaft, 1907, 40, 762), N:N'-diphenylethylene diamine (see Morley, ibid, 1879, 12, 1794), N:N'-diphenyl-N:N'-di(β-hydroxyethyl) ethylene diamine (obtainable by condensing N-β-hydroxyethylaniline with ethylene dibromide in the presence of sodium carbonate), N:N' - diphenylhexamethylene diamine (prepared by condensing hexamethylene dibromide with aniline in presence of sodium carbonate). A mixture of N-substituted diamines obtained by condensing o-toluidine and aniline with ethylene dichloride in the presence of sodium carbonate, may also be used.

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The N-substituted diamines of the present invention may be applied to the above mentioned materials, e. g., cellulose acetate artificial silk, in any convenient manner. The application of the N-substituted diamines may occur before, during or after the colouration of the material in question. For example, cellulose acetate artificial silk which has already been dyed, may be padded in an alcoholic solution of the desired N-substituted diamine, e. g., N:N'-diphenylethylene diamine. The cellulose acetate artificial silk is then squeezed to remove the superfluous alcoholic solution, and dried. The N:N'-diphenylethylene diamine may also be applied to the cellulose acetate artificial silk in similar manner before the cellulose acetate artificial silk has been dyed. In place of alcohol other organic solvents can be used to dissolve the N-substituted diamines, or the latter may be employed in the form of their dispersions in water. The aqueous dispersions for application to the cellulose acetate artificial silk are conveniently made by diluting with water either a strong aqueous dispersion or else a strong solution of the required N-substituted diamine in a water-miscible solvent containing a dispersing agent. For instance, a strong aqueous dispersion of N:N'-diphenylethylene diamine may be prepared by milling 20 parts thereof in 74 parts of water with 6 parts of disodium dinaphthylmethane disulphonate for 24 hours. This dispersion can then be diluted by adding a little thereof, if desired, to the actual dyebath in which the cellulose acetate artificial silk is to be dyed. In this manner the N:N'-diphenylethylene diamine is applied to the cellulose acetate artificial silk at the same time as it is dyed. In place of the strong aqueous dispersion of N:N'-diphenylethylene diamine just mentioned, a solution thereof in ethylene glycol monoethyl ether containing as dispersing

agent the condensation product of ethylene oxide (17 mols.) and cetyl alcohol (1 mol.) may be used. Other dispersing agents which can, for example, be used, are the condensation products from ethylene oxide (30 mols.) and cetyl alcohol (1 mol.), polyglyceryl ricinoleate, cetyl trimethylammonium bromide and sodium cetyl sulphate. Other organic solvents for the N-substituted diamines are, for instance, butyl alcohol and dioxan. The N-substituted diamines may also be brought into aqueous solution for application to the material which it is desired to treat, by dissolving them in the form of their salts, e. g., N:N'-diphenylethylene diamine hydrochloride. It is in that case, however, necessary to liberate the base, i. e., the diamine, by after-treatment with an alkali, e. g., sodium hydroxide. This is because the salts themselves are not effective in hindering or preventing the fading of the material by gas fumes. Instead of using sodium hydroxide, the material carrying the N-substituted diamine hydrochloride may be soaped after which it is found to have been given good protection against the effect of gas fumes.

The present N-substituted diamines are found to be effective in hindering or preventing the fading of dyed acetate artificial silk when only a small proportion, e. g., about 1%, thereof is applied. They have also, as already indicated above, the further advantage that they can be conveniently applied to cellulose acetate artificial silk at the same time as it is dyed. Moreover the present diamines are not toxic. They are also non-volatile and consequently do not tend to evaporate from the material to which they have been applied. Thus, for example, cellulose acetate artificial silk which has been treated with N:N'-dimethyl-N:N'-diphenylethylene diamine retains its resistance to the effect of gas fumes which has been conferred by the latter compound, indefinitely, when it is kept in storage. Furthermore the resistance to gas-fume fading imparted by the present N-substituted diamines is not removed when the fabric is treated with organic solvents used in dry cleaning, e. g., trichloroethylene. The inhibitory effect is also fast to perspiration and shows good stability to washing.

Although the fading of cellulose acetate artificial silk in the presence of gas fumes may occur somewhat slowly in practice, this effect can be hastened for the purpose of testing the efficiency of compounds designed to inhibit fading, by suspending two patterns of cellulose acetate artificial silk fabric, one treated with the compound it is wished to examine, one untreated, side by side inside a metal chamber connected with a chimney leading from a Bunsen burner, baffle plates being arranged in the metal chamber so as to cause the fumes from the burning gas to circulate over the fabrics. In this manner an effect can be produced in two or three hours which might take as many weeks to reach in, for example, the atmosphere of a warehouse, where gas fumes were present.

The following examples in which the parts are by weight, illustrate, without limiting, the present invention.

Example 1

100 parts of cellulose acetate artificial silk which has been dyed with 1% of 1:4:5:8-tetra-aminoanthraquinone, is padded at room temperature in 1000 parts of ethyl alcohol containing 10 parts of N:N'-diphenylethylene diamine. The

silk is then squeezed so that it retains its own weight of alcoholic solution. After drying, the so-treated material is found to have a much improved resistance to the fumes of burnt gas when compared with the untreated dyed material. This comparison is conveniently carried out by using the fumes from a Bunsen burner in the apparatus already referred to. When tested in this manner the untreated material exhibits very noticeable fading in the course of 3 hours, whereas the material which has been treated with N:N'-diphenylethylene diamine is only slightly affected.

Instead of N:N'-diphenylethylene diamine, N:N'-dimethyl-N:N'-diphenylethylene diamine can be employed with similar good results.

Example 2

20 parts of N:N'-diphenylethylene diamine are ball-milled in 74 parts of water with 6 parts of disodium dinaphthylmethane disulphonate for 24 hour. 5 parts of the resulting aqueous dispersion are added together with 1 part of 1:4:5:8-tetra-aminoanthraquinone and 9 parts of 50% Turkey red oil to 3000 parts of water. In the dyebath so constituted 100 parts of cellulose acetate artificial silk are dyed at 85° C. for 45 minutes. The material is then taken from the dyebath, rinsed well with water and dried. It is found to possess greatly improved fastness to burnt gas fumes when compared with cellulose acetate artificial silk which has been dyed in the same manner without the addition of the N:N'-diphenylethylene diamine.

Example 3

N:N'-diphenylethylene diamine is applied to cellulose acetate artificial silk whilst it is being dyed with 1:4:5:8-tetra-aminoanthraquinone as described in Example 2, except that the N:N'-diphenylethylene diamine is added to the dyebath in the form of a solution instead of an aqueous dispersion. Thus the dyebath is prepared as follows:

1 part of N:N'-diphenylethylene diamine is heated at 60° C. with 2 parts of the condensation product from ethylene oxide (17 mols.) and cetyl alcohol and 7 parts of ethylene glycol monoethyl ether until a clear yellow solution is obtained. This solution is added together with 1 part of 1:4:5:8-tetra-aminoanthraquinone and 9 parts of 50% Turkey red oil to 3000 parts of water.

Example 4

In place of the N:N'-diphenylethylene diamine used in Example 2, N:N'-dimethyl-N:N'-diphenylethylene diamine is employed, the dyebath being made up as follows:

25 parts of N:N'-dimethyl-N:N'-diphenylethylene diamine are warmed with 25 parts of the condensation product from ethylene oxide (17 mols.) and cetyl alcohol, 12.5 parts of the condensation product from ethylene oxide (30 mols.) and cetyl alcohol, and 37.5 parts of ethylene glycol monoethyl ether. 4 parts of the resulting solution are added together with 1 part of 1:4:5:8-tetra-aminoanthraquinone and 9 parts of 50% Turkey red oil to 3000 parts of water.

Example 5

1 part of N:N'-diphenylhexamethylene diamine is heated at 60° C. with 1.5 parts of the condensation product from ethylene oxide (17 mols.) and cetyl alcohol (1 mol.), and 7.5 parts of ethylene glycol monoethyl ether until a clear yellow solution is obtained. 10 parts of this solution are

added together with 1 part 1:4:5:8-tetra-amino-anthraquinone and 9 parts of 50% Turkey red oil to 300 parts of water. In the dyebath so prepared 100 parts of cellulose acetate artificial silk are dyed as described in Example 1. The dyed material is much faster to burnt gas fumes than the same material similarly dyed except that no N:N'-diphenylhexamethylene diamine is included in the dyebath.

We claim:

1. The process for improving the resistance to fume fading of colorations on materials comprised of cellulosic compounds from the group consisting of cellulose esters and cellulose ethers which comprises incorporating in said materials N:N'-diphenylethylene diamine.

2. The process for improving the resistance to fume fading of colorations on cellulose acetate materials which comprises incorporating in said materials N:N'-diphenylethylene diamine.

3. Dyed materials resistant to fume fading and comprised of cellulosic compounds from the group consisting of cellulose esters and cellulose ethers, and having incorporated therein N:N'-diphenylethylene diamine.

4. Dyed materials resistant to fume fading and comprised of cellulose acetate, and having incorporated therein N:N'-diphenylethylene diamine.

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