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DYED CELLULOSE MATERIALS OF IMPROVED FASTNESS TO LIGHT AND PROCESS OF PREPARING SAME

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It has been found that the fastness to light of materials containing cellulose which have been dyed with water-soluble dyestuffs containing at least one sulphonic acid or carboxyl group may be improved by treating the material before, during or after the dyeing process with organic derivatives of the acids of phosphorus, or with salts of these compounds. The water-soluble dyestuffs mentioned, which contain at least one sulphonic acid or carboxyl group, may also be denoted as water-soluble dyestuffs which contain at least one acid group.

As organic derivatives of the acids of phosphorus the following may be used: for example, esters of the acids of phosphorus with organic hydroxy compounds, also N-substituted amides or ester-amides of the acids of phosphorus, as well as phosphinic acids and phosphinous acids.

As esters of the acids of phosphorus the following may be used: for example, primary, secondary and tertiary esters of phosphoric acid, primary and secondary esters—that is to say, acid esters—especially in the form of salts, also esters of phosphorous acid. Phosphoric acid and phosphorous acid are examples of those acids of phosphorus which contain only hydrogen and oxygen in addition to phosphorus. To the organic derivatives of those acids of phosphorus which, besides phosphorus, contain only oxygen and hydrogen belong, for example, the esters of phosphoric acid and of phosphorous acid, also phosphinic acids and phosphinous acids. Substances which come into consideration are, for example, salts of monomethyl phosphate, of phosphoric acid monophenyl ester, of phosphoric acid diphenyl ester, of phosphoric acid mono-o-tolyl ester, of phosphoric acid mono-(1-methyl-5-chloro-3-hydroxybenzene) ester, of phosphoric acid mono-meta-xylenyl ester, of phosphoric acid mono-(4-hydroxydiphenyl) ester, as well as salts of monoethyl phosphite.

The salts of phosphoric acid phenyl ester and of phosphoric acid mono-orthotolyl ester mentioned above are examples of neutralized primary esters of phosphoric acid with hydroxy compounds of the benzene series. As neutralized esters of phosphoric acid with poly-hydroxy compounds of the benzene series, mention may be made of the salts of pyrocatechol-, resorcinol- or hydroquinone-diphosphoric acids, as well as of the salts of pyrogallol-phosphoric acids. The salts of p-carboxy-phenylphosphoric acid or of p-carbanyl-phenylphosphoric acid are examples of neutralized esters of phosphoric acid with hydroxy compounds of the benzene series which have at least one substituent containing a carbonyl group, which substituent is united to the benzene nucleus by a carbonyl group.

As N-substituted amides, use may be made, for example, of salts of phosphoric acid mono-anilide, of phosphoric acid di-anilide, of phosphoric acid mono-amide-mono-anilide.

Phenylphosphinic acid and phenylphosphinous acid may be mentioned as examples of those phosphinic and phosphinous acids which may be used in the present process.

Among the salts of organic derivatives of the acids of phosphorus, use may be made of salts of mono- and poly-valent metals, for example, salts of alkali and alkaline earth metals, of manganese, chromium and copper, etc. It is also possible to make use of organic derivatives of the acids of phosphorus which have been neutralized with amines as salts. It may be preferable to use as salts, metal complex salts of organic derivatives of acids of phosphorus.

The organic derivatives of acids of phosphorus and their salts which are to be used in the present process are either already known or may be prepared directly by analogous processes.

Dyed material coming into question in the present invention consists of, for example, dyed textile materials of vegetable origin, for example, materials derived from cotton, regenerated cellulose rayons, as well as paper and plastics.

The present process may be carried out by impregnating the cellulosic material, dyed with water-soluble dyestuffs containing at least one sulphonic acid or carboxyl group, with solutions of the organic derivatives of the acids of phosphorus or of their salts, preferably with aqueous solutions, so far as water soluble products are being used, and then drying. Should it be desirable to make use of difficultly soluble salts of polyvalent metals or of complex salts of heavy metals for the treatment of the fiber, the materials may be treated with easily soluble salts of the organic derivatives of the acids of phosphorus, for example, with alkali salts, and then after treating them with soluble salts of, for

example, polyvalent metals. In many cases, the addition may be made directly to the dyebath. Finally, the material to be treated may also be treated with the organic derivatives of acids of phosphorus or their salts before the dyeing process. The auxiliary products of the present process may also be added to dyed masses, for example, to solutions which serve for the manufacture of fibers or films—for example, solutions of viscose—or they may be added to such masses which are subsequently to be dyed. As will be seen from the foregoing, the treatment with the organic derivatives of acids of phosphorus, or with their salts, which is to be carried out at any desired stage of the dyeing process, forms a supplement to the dyeing process.

The dyed material which has been treated according to the present invention possesses an increased fastness to light over dyed material which has not been treated in this manner.

The products to be used according to the present invention may be applied alone, or in combination with other substances, such as salts—particularly those of weak acids, such as sodium acetate—and also together with solvents, soap-like substances, protective colloids, finishing, weighting, softening or dulling agents, and the like.

Example 1

Cotton which has been dyed with 2 per cent of Direct Sky Blue Green Shade (Color Index No. 518), or with 2 per cent of Rosanthrene Fast Bordeaux 2BL (Color Index page 365) is treated for 1 hour at room temperature with an aqueous solution containing 24.4 parts of phosphoric acid monophenyl ester in the form of its disodium salt for every 1000 parts by volume of treating liquor, after which it is well squeezed and dried for 1 hour at 55° C. The dyeing which has been treated in this manner has an appreciably better fastness to light than one which has not been so treated.

In place of the solution described above, a solution may be used that has been obtained by saponification of the dichloride of phosphoric acid phenyl ester with dilute caustic soda solution.

Further, the disodium salt of thiophosphoric acid monophenyl ester or the monosodium salt of phosphoric acid diphenyl ester may be used in a similar manner.

Example 2

Cotton which has been dyed with 3 per cent of Chlorantine Fast Red 7B (Schultz, Farbentabellen, Supplement I, page 79), or with 2 per cent of Chlorantine Red 8BN (Color Index No. 436), is treated in the manner described in Example 1 with an aqueous solution containing 25.1 parts of phosphoric acid mono-o-tolyl ester in the form of its disodium salt for every 1000 parts by volume of treating liquor. The fastness to light of the treated dyeing is better than that of an untreated dyeing.

The solution used can be obtained as follows:

30 parts of phosphoric acid mono-o-tolyl ester di-chloride are stirred with 300 parts by volume of water for 2 hours, after which time a clear solution is obtained which is then neutralized with normal caustic soda and is diluted to 1000 parts by volume wtih water.

Example 3

Cotton which has been dyed with 2 per cent of Direct Green B (Color Index No. 593) is treated in the method described in Example 1 with an aqueous solution containing 25.1 parts of phosphoric acid mono-p-tolyl ester in the form of its disodium salt for every 1000 parts by volume of treating liquor. The fastness to light of the dyeing so treated is better than that of an untreated dyeing.

The solution used can be prepared as follows:

30 parts of phosphoric acid mono-p-tolyl ester dichloride are stirred for 3 hours with 217 parts by volume of water, and the clear solution which is obtained is then neutralized with dilute caustic soda solution and is diluted to 1000 parts with water.

Example 4

The procedure of Example 1 is adopted with the exception that the solution of the neutralized phosphoric acid monophenyl ester is replaced by an aqueous solution of 3 per cent strength of the disodium salt of phosphoric acid mono-(3-hydroxy-5-chloro-1-methylbenzene) ester. The fastness to light of a dyeing thus treated is much better than that of one which has not been treated.

The solution used in aftertreating the dyeing is prepared in the following manner:

1 mol of 3-hydroxy-5-chloro-1-methylbenzene is heated to 130–150° C. with 1 mol of phosphorus oxychloride for 3 hours, 1 mol of hydrochloric acid gas being split off. Fractional distillation of the reaction mixture yields, after a small quantity of unchanged phosphorus oxychloride has passed over, a fraction which boils sharply between 141–146° C./13 mm., which consists of the chlorocresylphosphoric acid dichloride.

16.05 parts of chlorocresylphosphoric acid dichloride are stirred for 2 hours with 150 parts by volume of water, after which the mixture is neutralized with dilute caustic soda solution and water is added to yield a solution of 3 per cent strength.

Example 5

Cotton which has been dyed with 2 per cent of Direct Violet N (Color Index No. 394) is treated as described in Example 1 with an aqueous solution containing 30 parts of the disodium salt of phosphoric acid mono-m-xylenyl ester for every 1000 parts by volume of the treating liquor. The fastness to light of the treated dyeing is better than that of an untreated dyeing.

The solution used can be prepared as follows:—

1 mol of m-xylenol is heated for 3 hours at 140–165° C. with 1 mol of phosphorus oxychloride. After this time, the reaction mixture has split off 1 mol of hydrochloric acid gas. Fractional distillation yields, after a small quantity of phosphorus oxychloride has passed over, a fraction which boils sharply between 136 and 142° C./13 mm., which consists of the dichloride of xylenylphosphoric acid.

15 parts of xylenylphosphoric acid dichloride are stirred with 150 parts by volume of water for 2 hours, after which the mixture is neutralized with dilute caustic soda solution and water is added to yield a solution of 3 per cent strength.

Example 6

Cotton which has been dyed with 1 per cent of Direct Pink 3BN (Color Index Supplement, page 39) is treated as described in Example 1 with a solution of 3 per cent strength of the disodium salt of phosphoric acid mono-4-hydroxydiphenyl

ester. This treatment increases the fastness to light of the dyeing.

The solution used can be prepared as follows:

1 mol of 4-hydroxydiphenyl is heated to the boil under reflux with 4 mols of phosphorus oxychloride until 1 mol of hydrochloric acid gas has been split off, which requires about 9 hours. The excess of phosphorus oxychloride is removed from the reaction product by distillation in vacuo, when a white, friable mass is obtained as residue. 15 parts of this residue are now stirred for 2 hours with 245 parts by volume of caustic soda of normal strength, after which time the emulsion, which was at first strongly alkaline, has only a very weakly alkaline reaction to litmus.

The small quantity of undissolved substance which is still present is removed by filtration, and the filtrate is diluted with water to yield a 3 per cent solution.

Example 7

Cotton which has been dyed in the usual manner with 5 per cent of Rosanthrene Orange R (Color Index page 365) and developed with beta-naphthol, or which has been dyed with 2 per cent of Chlorantine Fast Orange G (Color Index Supplement page 32) is treated as described in Example 1 with a solution of 3 per cent strength of the disodium salt of phosphoric acid mono-anilide. The fastness to light of the dyeing treated in this manner is better than that of an untreated dyeing.

The solution used can be prepared as follows:—

15 parts of phosphoric acid mono-anilide dichloride are dissolved in 286 parts by volume of caustic soda solution of normal strength, and sufficient water is added to make a solution of 3 per cent strength.

Example 8

Cotton which has been dyed with 1 per cent of Direct Pink 3BN (Color Index Supplement page 39) is treated as described in Example 1 with a solution of 3 per cent strength of phenylphosphinic acid which has been neutralized with caustic soda.

The fastness to light of the dyeing is increased by this treatment.

The solution used may be prepared in the following manner:

15 parts of phenylphosphinic acid are pasted well in 200 parts by volume of water and are brought into solution by addition of 120 parts by volume of caustic soda solution of normal strength, after which water is added to make 500 parts by volume.

Example 9

Cotton which has been dyed with Direct Green B (Color Index No. 593) is treated as described in Example 1 with an aqueous solution of phenylphosphinous acid which has been neutralized with caustic soda. The material thus treated is faster to light than a similar untreated dyeing.

The solution used can be prepared as follows:

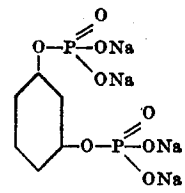
15 parts of phenylphosphinous acid are pasted well in 200 parts by volume of water and are brought into solution by addition of 124 parts by volume of caustic soda solution of normal strength, after which water is added to make 500 parts by volume.

Example 10

Cotton which has been dyed with 2 per cent of Chlorantine Red 8BN (Color Index No. 436) is treated at room temperature in an aqueous solution which contains 3 per cent of resorcinol-diphosphoric acid in the form of its tetra-sodium salt, as described in Example 1.

The fastness to light of the treated dyeing is appreciably better than that of an untreated similar dyeing.

The solution of the tetra-sodium salt of resorcinol diphosphoric acid, that is, the product of the formula



used above may be prepared as follows:

15 parts of resorcinol-diphosphoric acid tetrachloride are saponified by stirring with 100 parts by volume of water while cooling to yield resorcinol-diphosphoric acid. The clear solution obtained is then neutralized with 342 parts by volume of caustic soda solution of normal strength, and sufficient water is added to make 500 parts by volume.

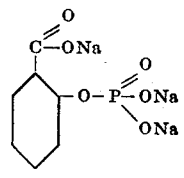
In a similar manner, the tetra-sodium salt of pyro-catechol-diphosphoric acid ester may be used.

Example 11

Cotton which has been dyed with 5 per cent of Carbide Black E (Color Index No. 581) is treated with a solution of 3 per cent strength of o-carboxyl-phenylphosphoric acid (neutralized with caustic soda) in the manner described in Example 1.

The fastness to light of the treated dyeing is appreciably better than that of an untreated dyeing.

The solution of o-carboxyphenylphosphoric acid, mentioned above, which has been neutralized with caustic soda, and which therefore contains the product of the formula



can be prepared as follows:

30 parts of o-chlorocarbonyl-phenylphosphoric acid di-chloride are rapidly covered with a layer consisting of a cooled solution of 26.4 parts of caustic soda in 250 parts by volume of water, and the whole is stirred for 8 hours whilst cooling with ice. The resulting solution is filtered to remove any traces of undissolved matter and water is added to make 1000 parts by volume.

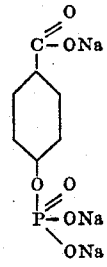
Example 12

Cotton which has been dyed with 1 per cent Direct Pink 3BN (Color Index Supplement, page 39) is treated as described in Example 1 with an aqueous solution of 3 per cent strength of p-carboxy-phenylphosphoric acid which has been neutralized with caustic soda.

The fastness to light of the treated dyeing is appreciably better than that of an untreated similar dyeing.

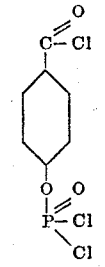
The solution of p-carboxyl-phenylphosphoric acid mentioned above, which has been neutralized

with caustic soda, and which therefore corresponds to the product of the formula



may be prepared as follows:

30 parts of p-chlorocarbonyl-phosphoric acid dichloride, of the formula



are saponified to the corresponding p-carboxyl-phenyl-phosphoric acid by stirring with 300 parts of water. After neutralizing with caustic soda, the solution is diluted with water to 1000 parts by volume.

Cotton which has been dyed with 2 per cent of Direct Sky Blue Green Shade (Color Index No. 518) is treated as described in Example 1 with a neutral aqueous solution of a compound which may be prepared as follows:

p-Chlorocarbonyl-phenylphosphoric acid dichloride is added to aqueous ammonia whilst cooling thoroughly. A finely crystalline product is precipitated, which has a constant melting point of 185–186° C. after recrystallization from water. To 50 parts of this product, a solution of 18.6 parts of caustic soda in 300 parts by volume of water is added, and the whole is allowed to stand for 4 hours at room temperature. After this time, the clear solution is acidified, when a new substance is obtained which may be recrystallized from water and which has a constant melting point of 159–161° C.

2.15 parts of this compound are made into a neutral solution in 100 parts by volume of water by addition of a few drops of soda solution. This solution which in all probability contains a sodium salt of an acid phosphoric acid ester of p-hydroxybenzoic acid amide, is used to impregnate the dyed material as described in Example 1.

The dyeing obtained by this treatment possesses appreciably better fastness to light than a similar untreated dyeing.

Example 14

Cotton which has been dyed with 2 per cent of Direct Pink 3BN (Color Index Supplement page 39) is treated in a bath containing 30 parts of the phosphoric acid ester of n-hexyl alcohol in the form of its sodium salt dissolved in 1000 parts by volume of water, the treatment lasting for five minutes. It is then squeezed so that it contains its own weight of the solution and is dried at 50–60° C. The cotton dyeing thus obtained has a better fastness to light than a similar untreated dyeing.

The sodium salt of the acid phosphoric acid ester of n-hexyl alcohol can be prepared in known manner, for example, by dropping 50 parts of phosphorus oxychloride into a mixture of 50 parts of n-hexyl alcohol and 50 parts of benzene, which is cooled with ice, and then keeping the mixture at a gentle boil on the water bath for 1 hour. The reaction mixture is then cooled and poured into ice-water, after which the benzene layer is washed several times with ice-water, neutralized with concentrated sodium carbonate solution and then, after the benzene has been removed by distillation, evaporated.

What we claim is:

1. A process for improving the fastness to light of materials containing cellulose which have been dyed with water-soluble dyestuffs containing at least one acid group, comprising supplementing the dyeing process by a treatment with a neutralized primary ester of phosphoric acid with a hydroxy compound of the benzene series.

2. A process for improving the fastness to light of materials containing cellulose which have been dyed with water-soluble dyestuffs containing at least one acid group, comprising supplementing the dyeing process by a treatment with a neutralized primary ester of phosphoric acid with a polyhydroxy compound of the benzene series.

3. A process for improving the fastness to light of materials containing cellulose which have been dyed with water-soluble dyestuffs containing at least one acid group, comprising supplementing the dyeing process by a treatment with a neutralized solution of resorcinol-diphosphoric acid.

4. A process for improving the fastness to light of materials containing cellulose which have been dyed with water-soluble dyestuffs containing at least one acid group, comprising supplementing the dyeing process by a treatment with a neutralized primary ester of phosphoric acid with a hydroxy compound of the benzene series which contains at least one substituent containing a carbonyl group, which substituent is bound to the benzene radical through a carbonyl group.

5. A process for improving the fastness to light of materials containing cellulose which have been dyed with water-soluble dyestuffs containing at least one acid group, comprising supplementing the dyeing process by a treatment with a neutralized solution of p-carboxy-phenyl-phosphoric acid.

6. A process for improving the fastness to light of materials containing cellulose which have been dyed with water-soluble dyestuffs containing at least one acid group, comprising supplementing the dyeing process by a treatment with a neutralized solution of a phosphoric acid derivative obtainable by treating p-chlorocarbonyl-phenyl-phosphoric acid dichloride with ammonia, and reacting the product thus obtained with sodium hydroxide solution.

7. Cellulose materials which contain a neutralized primary ester of phosphoric acid with a hydroxy compound of the benzene series, and which are dyed with a water-soluble dyestuff containing at least one acid group.

8. Cellulose materials which contain a neutralized primary ester of phosphoric acid with a polyhydroxy compound of the benzene series, and which are dyed with a water-soluble dyestuff containing at least one acid group.

9. Cellulose materials which contain a neutralized resorcinol-diphosphoric acid, and which are dyed with a water-soluble dyestuff containing at least one acid group.

10. Cellulose materials which contain a neu-

tralized primary ester of phosphoric acid with a hydroxy compound of the benzene series which contains at least one substituent containing a carbonyl group, which substituent is bound to the benzene radical through a carbonyl group, and which are dyed with a water-soluble dyestuff containing at least one acid group.

11. Cellulose materials which contain a neutralized p-carboxy-phenylphosphoric acid, and which are dyed with a water-soluble dyestuff containing at least one acid group.

12. Cellulose materials which contain a neutralized phosphoric acid derivative obtainable by treating p-chloro-carbonyl-phenyl-phosphoric acid dichloride with ammonia, and reacting the product thus obtained with sodium hydroxide solution, and which are dyed with a water-soluble dyestuff containing at least one acid group.

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