NEW TEXTILE TREATMENT PROCESS


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This invention relates to a textile treatment process and more particularly it relates to a process for the colouration of textile materials comprising protein or artificial fibres in shades having extremely good fastness to wet treatments.

It has previously been proposed to improve the fastness to wet treatments of textile materials which have been dyed with a dyestuff containing at least one reactive hydrogen atom, by treating the dyed textile material with a heterocyclic substance containing in the heterocyclic ring at least one grouping of the formula

\[ N=\text{C(halogen)} \]

In particular there has been described the treatment of a dyed textile material with an aqueous emulsion of a solution of cyanuric chloride or 2,4,6-trichloroquinazoline line in benzene and carbon tetrachloride.

The previously described processes however are difficult to apply in practice because of the toxic hazard involved in the use of these organic solvents. Furthermore the fastness to wet treatment of textile materials so treated is usually uneven.

It has now been found that the textile materials hereinafter defined, especially those made from protein or synthetic protein fibres, may be coloured satisfactorily in shades having a high fastness to wet treatments when there are used in the colouration process dyestuffs containing a reactive amino group as hereinafter defined and the treatment with the dyestuff is carried out in conjunction with a treatment with an aqueous solution of a water soluble heterocyclic compound containing at least one heterocyclic ring or the like, thus eliminating the toxic hazards of the previously described processes and giving a uniform improvement in fastness to wet treatments.

For the purpose of this invention, a reactive amino group is one which contains a hydrogen atom which is readily replaced by treating the dyestuff with cyanuric chloride at 20° C. in aqueous medium.

Suitable dyestuffs include, for example, Naphthol Green A (Colour Index No. 20495), Solochrome Yellow 2GN (Colour Index No. 14045), Duranol Brilliant Blue CB (Colour Index No. 64414), 1,8-dihydroxy-4:5:4:5-diminoantraquinone-2:7-disulphonic acid, Solochrome Brown EB (Colour Index No. 20110), Chlorazol Black BH (Colour Index No. 22390), Chlorazol Brown MR (Colour Index No. 22311), Chlorazol Sky Blue FF (Colour Index No. 24410), Ultralux Orange R (Colour Index No. 18170), p-aminophenylazoacetic acid and the chromium complex of 3:5-dinitro-2:4-diamino-2-hydroxyazobenzene-5-sulphonic acid.

The Colour Index numbers are those given in the second edition of the Colour Index, published jointly in 1957 by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists.

The textile materials treated in the process of the invention are those obtained from natural protein and artificially-produced fibres, for example wool, silk, ethers and esters of cellulose, especially cellulose acetate, polyamides for example nylon, polyacrylonitrile and its co-polymers and polyvinylalcohol.

According to the present invention, therefore, there is provided a process for the treatment of textile materials as hereinafter defined which comprises treating the textile material with an aqueous solution of a water soluble heterocyclic compound containing at least once the grouping of the formula \( N=\text{C(halogen)} \) in the ring, and with a dyestuff containing at least one reactive amino group as hereinafter defined.

Suitable water-soluble heterocyclic compounds for use in the above process may be obtained for example by interaction of a poly-halogeno heterocyclic compound such as a trihalogenopyrimidine or a cyanuric halide, especially cyanuric chloride, with a compound which contains at least one water-solubilising group, for example sulphonic acid, carboxylic acid, or sulphate or phosphate ester group (or salts thereof) and which also contains at least one grouping, for example hydroxyl, thiol or amino, known to be capable of interaction with the halogen of the heterocyclic compound.

Especially suitable compounds for use in the process of the invention may be obtained by interaction of a cyanuric halide, preferably the chloride, with a primary or secondary amine containing at least one water-solubilising group, under conditions such that at least one halogen atom or preferably two halogen atoms, remain attached to the triazine ring. Suitable conditions for such reactions are well known from the literature.

Thus, there may be used the primary and secondary condensation products of cyanuric chloride and such amines as 1-naphthylamine-5- and -7-sulphonic acids, 2-naphthylamine-6- and -7-sulphonic acids, 2-methylaminonaphthalene-6-sulphonic acid, benzidine disulphonic acid, p-aminophenyl-beta-hydroxy-ethyl ether sulphuric ester, 2-naphthylamine-1:6-, 4:8-, 5:7- and 6:8-disulphonic acids, 1-naphthylamine-4:6:8-trisulphonic acid, sulphonic acid, 3-amino-5-sulpho-2-hydroxybenzoic acid, p-phenylene diamine sulphonic acid, orthilianic acid, malonic acid, m-phenylene diamine-4-sulphonic acid, aminomethane phosphoric acid, aminophenyl trimethylemmonium bromide, p-aminobenzoic acid, taurine, N-methyltaurine, N-phosphylglycine, 4:4'diamino-stilbene-2:2'disulphonic acid, and 2-amino-5-naphthol-6-sulphonic acid. There may also be used the primary and secondary condensation products of cyanuric chloride and hydroxy and mercapto compounds especially 2-thiophenol-6-sulphonic acid. The following list names typical examples of heterocyclic compounds which may be used:

1. (2':4':2'-dichloro-s-triazinylamino)naphthalene-7-sulphonic acid,
2. (2':4':2'-dichloro-s-triazinylamino)naphthalene-5-sulphonic acid,
3. (2':4':2'-dichloro-s-triazinylamino)naphthalene-7-sulphonic acid,
4. (2':4':2'-dichloro-s-triazinylamino)methylenonapthalene-6-sulphonic acid,
5. 4-amino-4':4'-dichloro-s-triazinylamino)diphenyl disulphonic acid,
6. 4'-biphenyl-s-triazinylamino)diphenyl disulphonic acid,
7. (2':4'':4'-dichloro-s-triazinylamino)phenoxo-beta-ethoxy sodium sulphate,
3-(2',4'-dichloro-s-triazinylamino) benzene sulphonate acid, 2-(2',4'-dichloro-s-triazinylamino)naphthalene-4-sulphonic acid, 2-(2',4'-dichloro-s-triazinylamino) methylene disulphonic acid, 2-(2',4'-dichloro-s-triazinylamino)naphthalene-5-sulphonic acid, 4-(2,4-dichloro-6-sulphonic acid)-s-triazine, 4-(2,4-dichloro-6-(carboxymethylamino)s-triazine, 2,4-dichloro-6-sulphonyl chloride, 2,4-dichloro-6-sulphamido-s-triazine, 2,4-dichloro-6-sulphonyl-naphthalene-2-sulphonic acid, 4,4-bis(2',4'-dichloro-s-triazinylamino) benzene sulphonate acid, and 2,5-bis(2',5'-dichloro-s-triazinylamino) benzene sulphonate acid. However the heterocyclic compounds are not limited in use to the colourless compounds obtained from the starting materials just mentioned. There may also be used a coloured heterocyclic compound containing two groups of the type —N=C(1-halo)- thereby obtaining being secondary or tertiary shades having good fastness to washing. Such shades with good washing fastness cannot at present be easily obtained with dyesuffs at present commercially available which either contain an amine group or one or more groups of the type —N=C(1-halo). The particular shades of dyestuff and coloured heterocyclic compound used should be chosen in accordance with the commonly accepted methods of mixing dyestuffs having primary or secondary shades in order to obtain secondary or tertiary shades. Suitable coloured heterocyclic compounds for example of the azo anthraquinone, nitro and phthalocyanine series are described in British specifications Nos. 209,723, 298,484, 772,030, 774,925, 775,508, 780,591, 781,930, 785,120, and 785,222, and in Belgian specifications Nos. 552,910, 556,092, 557,162 and 558,390. When it is desired to colour the entire surface of the material, the dyestuff, especially if it is a dyestuff having poor affinity for the material being coloured, such as a disperse dyestuff on wool or an acid dyestuff on cellulose acetate, may be applied by padding the textile material in an aqueous solution or suspension of the dyestuff. Dyestuffs of the type commonly used for dying the textile material may be applied by the commonly used techniques. For the local colouration of the textile material the dyestuff may be applied from a thickened printing paste. The water-soluble heterocyclic compound may be applied by padding the textile material in an aqueous solution of the heterocyclic compound in a pretreatment or aftertreatment step and may be added to the dyebath or printing paste containing the dyestuff. The pretreatment or aftertreatment step may alternatively comprise a treatment in a neutral or slightly acid solution of the heterocyclic compound at a temperature of between 50 and 100° C for a period of between 10 and 60 minutes. The solutions, suspensions and printing pastes containing dyestuff and/or heterocyclic compound may also contain the adjuvants commonly used in dyeing and padding solutions and suspensions and textile printing pastes. Such adjuvants include, for example, migration inhibitors such as ethers of cellulose, sodium chloride and sodium sulphate, wetting agents such as condensates of ethylene oxide with fatty alcohols and phenols, sulphonated fatty alcohols and sulphonated oils, solution aids such as urea and thioglycol and thickening agents such as gum arabic, starch, gum tragacanth and preferably sodium alginate.

When the dyestuff or heterocyclic compound used in the process contains a metal-complex forming system such as a o-hydroxy carboxylic acid or a o,o'-dihydroxy-azo or benzene grouping, the new process may advantageously incorporate a treatment with a metal-yielding agent such as copper sulphate, cobalt sulphate, nickel sulphate, ferrous sulphate or chromium acetate, in order to improve the fastness to light of the resultant colourations. The (2',4'-dichloro-s-triazinyl) derivative of 3-amino-2-hydroxy-5-sulphobenzene acid is particularly useful so that this treatment may be carried out. The textile materials coloured by the new process are advantageously scoured in soap or detergent solutions, in order to improve still further the fastness to washing.

The process of the invention enables protein, and artificial textile materials to be coloured in a wide variety of shades having far greater fastness to washing than the shades obtainable from the same dyestuffs by the commonly-used techniques. The invention is illustrated but not limited by the following examples in which parts are by weight:

Example 1

<table>
<thead>
<tr>
<th>Parts</th>
<th>Weight</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td></td>
<td>Duranol Brilliant Blue CB200 paste fine</td>
</tr>
<tr>
<td>4,000</td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>Methylated spirits 50%</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Sodium alginate (5% aqueous solution)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Sodium salt of sulphonated sperm oil</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>Sodium m-nitrobenzene sulphonate</td>
</tr>
</tbody>
</table>

The paste is applied to the treated nylon fabric by roller printing. The fabric is dried at 70° C, steamed for 30 minutes at atmospheric pressure, rinsed in water and washed for 10 minutes at 60° C. In 4,000 parts of water containing 8 parts of soap, and dried. The blue print obtained possesses higher fastness to washing than a print obtained using the above print paste on untreated nylon.

Example 2

A printing paste is made by mixing together 10 parts of Duranol Brilliant Blue CB200 paste fine, 10 parts of urea and 20 parts of water, then adding a solution of 1 part of sodium 2-(2',4'-dichloro-s-triazinylamino) naphthalene-6-sulphonate in 24 parts of water and finally 35 parts of a 5% solution of sodium alginate. The printing paste is applied to wool and the wool is then dried, steamed for 10 minutes, rinsed in cold water, treated for 10 minutes at 60° C in a 0.3% aqueous solution of a detergent mixture consisting of sulphonated fatty alcohol and alkyl phenols condensed with ethylene oxide, rinsed again and dried.

Blue prints are obtained which are stronger than those obtained from a printing paste from which the sodium 2-(2',4'-dichloro-s-triazinylamino) naphthalene-6-sulphonate has been omitted. Similar results are obtained if chlorinated wool, silk or nylon is used in place of the wool.
Example 3
Silk cloth is padded in a 5% aqueous solution of sodium 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate and the cloth is squeezed through rollers to remove excess liquid and is then dried. The cloth is then padded in a 0.5% aqueous suspension of Duranol Brilliant Blue CB and squeezed and dried. It is then "acid-steamed" (suspended in a vessel containing steam and the vapour of acetic acid) for 15 minutes.

The blue dyeing so obtained is superior in washing fastness to a dyeing of similar depth of Duranol Brilliant Blue CB on silk which has not had the pretreatment step described above.

A similar effect is obtained if nylon cloth or acetate rayon cloth is used in place of the silk.

Example 4
If in the method described in Example 3, the sodium 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate is replaced by the dyestuff described in Example 1 of United Kingdom specification No. 774,925, the silk and nylon cloths are dyed green shades having very good fastness to washing.

Example 5
20 parts of silk are immersed in 1200 parts of water containing 1 part of sodium - 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate, 1 part of Duranol Brilliant Blue CB and 0.6 part of oleyl sodium sulphate.

The bath is heated to 65° C. and held at this temperature for 20 minutes. 0.1 part of 85% formic acid is added and the bath is heated to 95° C. 0.7 part of 85% formic acid is added and the treatment is continued for 1 hour at 95° C.

The fastness to washing of the blue dyeing so obtained is much superior to one carried out without the addition of the sodium 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate.

Nylon can be dyed in similar manner, except that the bath is first heated to 85° C. instead of 65° C. A similar effect is obtained if the formic acid is added to the bath before heating. A weaker dyeing is obtained, but the fastness to washing is again superior to a dyeing carried out without adding the sodium 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate.

Example 6
If the sodium 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate used in Example 5 is replaced by the dyestuff described in Example 1 of United Kingdom specification No. 774,925, the cloth, silk or nylon as the case may be, is dyed a green shade of very good fastness to washing.

Example 7
20 parts of cellulose acetate are immersed in 1200 parts of water containing 1 part of 4-(2'-4'-dichloro-s-triazinylamino)phenoxy-beta-ethylenodium sulphate, 1 part of Duranol Brilliant Blue CB and 0.6 part of oleyl sodium sulphate and the bath is heated to 85° C. After 30 minutes, 8 parts of sodium chloride are added and the treatment is continued for 45 minutes.

A pale blue dyeing is obtained, having superior fastness to washing and somewhat redder in shade than a dyeing carried out without the addition of the 4-(2'-4'-dichloro-s-triazinylamino)phenoxy-beta-ethylenodium sulphate.

If in place of this compound there is used the dyestuff described in Example 1 of United Kingdom specification No. 774,925 a similar improvement in washing fastness is obtained.

Example 8
A printing paste is made up by mixing together 10 parts of Duranol Brilliant Blue CB, 42 parts of water, 40 parts of a 5% aqueous solution of sodium alginate, 5 parts of 50% aqueous ethanol, 2 parts of a wetting agent consisting of an aqueous emulsion of sulphonated sperm oil and pine oil, and 1 part of sodium m-nitrobenzene sulphonate.

This paste is applied to continuous filament nylon twill fabric by roller and the print is dried and steamed for 30 minutes. The fabric is padded in a 5% aqueous solution of sodium 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate and 2% of the wetting agent mentioned above, squeezed between rollers so that it retains only its own weight of solution, and is then dried at 105° C. by contact with the surface of a steam-heated drum.

The nylon is then steamed for 10 minutes, rinsed, washed, and rinsed again and dried as described in Example 1. The blue print obtained has better fastness to washing than a print which has not been aftertreated in the sodium 2-(2'-4'-dichloro-s-triazinylamino)naphthalene-6-sulphonate.

If cellulose acetate sateen fabric is used in place of the nylon, a similar effect is obtained.

Example 9
100 parts of nylon are immersed in 4000 parts of water at 95° C. containing 4 parts of cetyl sodium sulphate and 2 parts of tetraminoanthraquinone. After 30 minutes the nylon is rinsed and treated for 30 minutes in 4000 parts of water at 95° C. containing 4 parts of formic acid (85%), and 2 parts of the product obtained by interacting equimolecular proportions of sodium 2-naphthylamine-6-sulphonate and cyanuric chloride. The nylon is then "soaped" for 5 minutes at 85° C. in a bath containing an alkaline detergent. A blue dyeing of excellent wet fastness is obtained.

If the "soaping" treatment is omitted in the above example, a similar result is obtained.

Example 10
The process described in Example 9 is repeated, using 1 part of the dye formed by coupling diazotised p-nitroaniline with aniline in place of the tetraminoanthraquinone. A reddish yellow dyeing of excellent wet fastness results.

Other dyestuffs which may be used in place of the tetraminoanthraquinone are 4-amino-4'-dimethylanilinoazobenzene, 4-(4'-aminophenylazo)-1-aminoazophenol and 4,4'-diamino-5-dimethoxy-2-methylazobenzene (all of which give yellow shades), 1:4-diamino-2-methoxyanthraquinone (which gives a red shade), 5-nitro-1:4-diaminoanthraquinone, 1:4:5-triaminoanthraquinone and 1:4-diaminoanthraquinone (all of which give violet shades), and 1:5-diamino-4:8-di-(methylamino)-anthraquinone and 1:8-di-hydroxy-4:5-di-(beta-hydroxyethylamino)-anthraquinone (both of which give blue shades).

Example 11
The process described in Example 9 is repeated, using, in place of the product obtained by interacting equimolecular proportions of sodium 2-naphthylamine-6-sulphonate and cyanuric chloride, an equal weight of the product obtained by interacting equimolecular proportions of sodium benzidine mono-sulphonate and cyanuric chloride. A blue dyeing of excellent wet fastness results.

Example 12
The process described in Example 9 is repeated, using, in place of the product obtained by interacting equimolecular proportions of sodium 2-naphthylamine-6-sulphonate and cyanuric chloride, an equal weight of di-sodium N,N'-bis-(2'-chloro-4'-hydroxy-s-triazinylamino)-benzidine-2:2'-disulphonate. A blue dyeing of excellent wet fastness results.

Example 13
The process described in Example 9 is repeated, using,
in place of the product obtained by interacting equimolecular proportions of sodium 2-naphthylamine-6-sulphonate and cyanuric chloride, an equal weight of the product obtained by interacting equimolecular proportions of cyanuric chloride and disodium 2-aminoanthraquinone-4:8-disulphonate. A blue dyeing of excellent wet fastness results.

Example 14
The process described in Example 9 is repeated, but replacing the 4 parts of formic acid used therein by 3 parts of sulphuric acid. A blue dyeing of excellent wet fastness results.

Example 15
The process described in Example 9 is repeated but the nylon is replaced by an equal weight of a modified polyacrylonitrile fabric. A blue dyeing of excellent wet fastness results.

Example 16
The process described in Example 9 is repeated but the nylon is replaced by an equal weight of wool. A blue dyeing of excellent wet fastness results.

Example 17
The process described in Example 9 is repeated but the nylon is replaced by an equal weight of silk. A blue dyeing of excellent wet fastness results.

Example 18
Nylon is dyed with tetraamino-anthraquinone as described in Example 9, and after-treated as described therein but using 3-(2:4'-dichloro-s-triazinylamino)-2-hydroxy-5-sulphobenzoeic acid in place of the product obtained by interacting equimolecular proportions of sodium 2-naphthylamine-6-sulphonate and cyanuric chloride. The dyed fabric has a light fastness of 5 measured on the standard scale adopted by the Society of Dyers and Colourists.

The fabric is then steamed for 15 minutes at atmospheric pressure, washed for 5 minutes at 85°C in a 0.5% aqueous solution of the wetting agent mentioned in the first paragraph, rinsed in water and dried.

A fast yellow dyeing is obtained.

What we claim is:
1. A process for the coloration of textile material made from fibers of the class consisting of protein and artificially-produced fibers, which comprises treating said textile material with an aqueous solution of a heterocyclic compound selected from the class consisting of dihalogeno-triazine and dihalogeno-pyrimidine water-soluble compounds and with a dyestuff having an amino group-hydrogen atom which can be readily replaced by treatment with cyanuric chloride aqueous medium at 20°C.

2. Process as claimed in claim 1 characterised in that the heterocyclic compound contains a dihalogeno-triazine group.

3. Process as claimed in claim 1 characterised in that the heterocyclic compound contains a dichloro-s-triazine group.

4. Process as claimed in claim 1 characterised in that the reactive amino group present in said dyestuff contains two hydrogen atoms attached to the nitrogen atom.

5. Process as claimed in claim 1 characterised in that the treatment of the textile material with the heterocyclic compound and dyestuff is carried out by padding the textile material in an aqueous solution of the heterocyclic compound also containing the dyestuff, and the treated textile material is then subjected to an elevated temperature.

6. Process as claimed in claim 1 characterised in that the treatment of the textile material with the heterocyclic compound and dyestuff is carried out by printing the textile material with a single printing paste containing the dyestuff and the heterocyclic compound, and the printed textile material is then subjected to an elevated temperature.

7. Process as claimed in claim 1 characterised in that the textile material is first treated with an aqueous solution of the heterocyclic compound and dried, the dried textile material is printed with a printing paste containing the dyestuff and the textile material is thereafter subjected to an elevated temperature.

8. Process as claimed in claim 1 characterised in that the textile material is first treated with an aqueous solution of the heterocyclic compound and dried, the dried textile material is padded in an aqueous medium containing the dyestuff and dried and the textile material is then subjected to an elevated temperature.

9. Process as claimed in claim 1 characterised in that the textile material is first dyed and the dyed textile material is treated with an aqueous solution of the heterocyclic compound.

10. Process as claimed in claim 1 characterised in that the dyestuff used contains a metal-complex forming system and the process incorporates a treatment with a metal-yielding agent.

References Cited in the file of this patent
UNITED STATES PATENTS
2,820,785 Zollinger 21 Jan. 1958
FOREIGN PATENTS
209,723 Great Britain 23 Mar. 1925