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PROCESS FOR COLORING CELLULOSE WITH NEW TRIAZINE DYESTUFFS

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This invention relates to new colouring matters and their use and more particularly it relates to new colouring matters containing s-triazine rings, and to the colouration process to be used for their application to cellulosic textile materials.

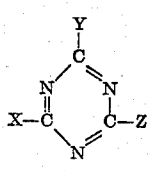
It has previously been proposed to manufacture dyestuffs, for example of the azo and anthraquinone series, containing one or more s-triazine nuclei and to use these dyestuffs, amongst other uses, as simple direct dyestuffs for the dyeing of cellulose. As is well known to those skilled in the art, direct dyestuffs as a class do not have very good fastness to severe washing treatments as compared with vat dyestuffs and other temporarily solubilised dyestuffs.

The basis of the present invention resides in the observation that certain new water-soluble s-triazine compounds have the valuable property that they may be used to colour cellulosic textile materials in shades having an excellent fastness to severe washing treatments approaching, and in most cases equalling, the wash-fastness properties of vat dyestuffs, provided that the colouration process is carried out in conjunction with a treatment with an alkaline substance.

The new s-triazines forming the subject of this invention are those containing on the one hand at least one grouping of the class consisting of negatively-substituted aryloxy, unsubstituted arylthio and substituted arylthio, and on the other hand the radical of a coloured compound or the radical of a colourless compound which contains at least one grouping known from the art or used in practice to enable colourless compounds to be converted in situ on a textile material to a coloured compound, said radical being attached to the triazine nucleus through a nitrogen atom.

It is believed, although it has not been fully proved, that the reason for obtaining colourations having such high resistance to washing treatments from the new colouring matters is that, when applied in conjunction with an alkaline agent, the new colouring matters react chemically with the textile material. It is believed that the aryloxy or arylthio grouping is removed and a triazinyl ester of cellulose is formed.

Thus, according to the present invention there are provided new water soluble colouring matters represented by the formula:



wherein X represents a grouping wherein the radical of a coloured compound, or the radical of a colourless compound which contains groupings known from the art or from use in practice to enable colourless compounds to be convertible in situ on a textile material to a coloured compound, is attached to a nitrogen atom which is also attached to the carbon atom of the triazine nucleus,

Y represents a negatively-substituted aryloxy grouping or a substituted or unsubstituted arylthio grouping, and

Z represents a substituent connected to the triazine nucleus through a carbon, nitrogen, oxygen or sulphur atom.

The solubilising groups, for example sulphonic acid or carboxylic acid groups, in the new colouring matters may be present in any of the groupings or substituents represented by X, Y, and Z in the above formula.

The nitrogen atom in X which is attached to a carbon atom of the triazine ring may be attached by one link or by two links to the remainder of the dyestuff or dyestuff intermediate molecule. When it is attached by two links, it may, for example, form part of a saturated heterocyclic ring such as a piperazine ring. When it is attached by one link, the third substituent attached to the nitrogen atom may be, for example, a hydrogen atom, alkyl group, aralkyl or cycloalkyl group.

The substituent represented by Z may be a grouping of the types represented by X or Y, and if so, Z may represent the same grouping as one of X and Y or it may represent a grouping different from the groupings represented by X and Y. When Z does not represent a grouping of the types represented by X or Y, it may represent, for example, an alkyl, aryl, alkoxy, substituted alkoxy, cycloalkoxy, aralkoxy, unsubstituted aryloxy, alkyl mercapto, amino or a mono- or di-substituted amino group which does not fall into the class represented by X.

The groupings X and Z in the above formula may contain a s-triazinylamino grouping wherein the triazine nucleus is substituted by at least one negatively substituted aryloxy grouping so that the new colouring matter then contains more than one such s-triazinylamino grouping.

The preferred new colouring matters are those in which both Y and Z are the same and represent phenoxy and thiophenoxy groups substituted by at least one sulphonic acid group.

The new colouring matters may be obtained by reacting together a triazine containing more than one halogen atom attached to the carbon atoms thereof, a negatively substituted hydroxy-aryl compound or a substituted or unsubstituted mercaptoaryl compound and a compound which is characterised first in that it contains one or more amino or mono-substituted amino groups and secondly in that it is coloured or, if colourless it also contains groupings known from the art or used in practice to enable a colourless substance to be converted to a coloured substance, in such proportions and under such conditions that no halogen atoms are left attached to the triazine nucleus. This manufacturing process forms a further feature of the invention.

Thus, as examples of suitable triazines which may be used there may be mentioned cyanuric chloride, cyanuric bromide, 2-phenyl-4:6-dichlorotriazine, 2-methyl-4:6-dichlorotriazine, 2-methoxy-4:6-dichlorotriazine, 2-beta-chloroethoxy-4:6-dichlorotriazine, 2-amino-4:6-dichlorotriazine, 2-anilino-4:6-dichlorotriazine, 2-phenoxy-4:6-dichlorotriazine, 2-ethoxy-4:6-dichlorotriazine, 2-p-methylphenoxy-4:6-dichlorotriazine, 2-methylamino-4:6-dichlorotriazine, 2-dimethylamino-4:6-dichlorotriazine, 2-diethylamino-4:6-dichlorotriazine, 2-isopropylamino-4:6-dichlorotriazine, 2-p-chloroanilino-4:6-dichlorotriazine, 2-N-methylanilino-4:6-dichlorotriazine and 2-cyclohexylamino-4:6-dichlorotriazine.

As examples of negatively substituted hydroxy-aryl compounds which may be used there may be mentioned phenol-4-sulphonic acid, phenol-3-sulphonic acid, 2-nitrophenol-4-sulphonic acid, 2-chlorophenol-4-sulphonic acid,

4-methylphenol-2-sulphonic acid, phenol-2:4-disulphonic acid, phenol-3:5-disulphonic acid, phenol-3- or 4-carboxylic acid.

As examples of substituted or unsubstituted mercapto-aryl compounds which may be used there may be mentioned thiophenol, thiophenol-3-sulphonic acid, thiophenol-4-sulphonic acid, 2-thionaphthol-6:8-disulphonic acid, 2-thionaphthol-6-sulphonic acid, p-nitrothiophenol, p-chlorothiophenol and p-thiocresol.

As examples of the monosubstituted amino groups which may be present in the compounds used in the above process there may be mentioned alkylamino for example methylamino, ethylamino, propylamino and butylamino, beta-hydroxyethylamino, beta-sulphoethylamino, beta-sulphatoethylamino, beta-chloroethylamino, gamma-chloro-beta-hydroxypropylamino and beta-carboxyethylamino, aralkylamino, for example benzylamino and cycloalkylamino such as cyclohexylamino.

The said compounds used in the above process are further characterised in that they are coloured or, if colourless, they contain groupings known from the art or used in practice to enable a colourless substance to be converted to a coloured substance.

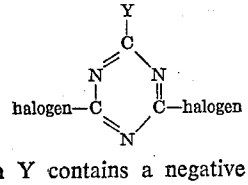
Suitable compounds include, for example, dyestuffs of the various series containing amino-groups, such as nitro-dyestuffs, azo-dyestuffs, including thiazole dyestuffs, azoxy-stilbene-dyestuffs and pyrazolone or hydrazone dyestuffs, di- and tri-aryl-methane dyestuffs, acridine-, oxyazine-, thiazine- and azine-dyestuffs, indigoids, aminoanthraquinones, aminoanthraquinone-dyestuffs, phthalocyanine dyestuffs, aromatic diamines, aminophenols, aminonaphthols and N- and O-acidyl or alkyl, aralkyl or aryl-derivatives of these.

The process may conveniently be carried out in a liquid medium preferably in an aqueous medium, that is, in water or in a mixture of water and a water miscible organic liquid such as acetone, dioxan or dimethylformamide. When the process is carried out in an aqueous medium, the negatively-substituted hydroxy-aryl compound or substituted or unsubstituted mercapto-aryl compound is preferably reacted in the form of its alkali metal salt. An acid-binding agent, preferably a carbonate or bicarbonate, may, if desired, be added to the reaction medium.

Certain of the triazines usable in the process, especially those wherein Z in the above formula represents an amino or substituted amino group, may readily be obtained by reacting a cyanuric halide with one molecular proportion of ammonia or an amine in aqueous media similar to those used in the process of the invention. Such starting materials may, if desired, be manufactured in this manner and then reacted in situ.

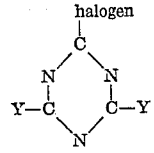
The process is preferably carried out in two stages, first reacting together the triazine and one of the two other reactants and then treating the product so obtained with the third reactant. If desired, the intermediate product obtained by the first stage may be isolated and purified before reacting it with the third reactant. Alternatively, the intermediate product may be further reacted in situ.

In considering in which order to react together the various starting materials usable in the above process, it should be noted that it has been found unexpectedly difficult to obtain in a pure state intermediate primary condensation products of the type:



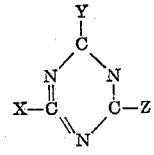
especially when Y contains a negative group which is a water-solubilising group, since the interaction of equimolecular proportions of a cyanuric halide and, for example, a sulphonated or carboxy-phenol or thiophenol gives rise to a complex mixture containing unreacted cyanuric halide and both primary and secondary condensation products.

On the other hand, the intermediate secondary condensation products of the type:



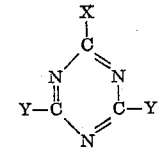
may readily be obtained by reacting together one molecular proportion of a cyanuric halide and two molecular proportions of a suitable hydroxy-aryl or mercapto-aryl compound chosen in accordance with the invention.

Thus where it is desired to obtain a colouring matter of the type:



where X and Y have the meanings given above, and Z differs from Y but may be of the same type as X, it is preferred to carry out the condensation step using the hydroxy-aryl or mercapto-aryl compound Y—H as the final step.

However, where the desired colouring matter is of the form:



wherein X and Y have the meanings given above, the desired product may be obtained by condensing one molecular proportion of a cyanuric halide with about one molecular proportion of a colouring matter XH and about two molecular proportions of the hydroxyaryl or mercaptoaryl compound Y—H in either order.

It is frequently found desirable, especially when the process is carried out in an aqueous medium, to use a slight excess of the cyanuric halide over the theoretical quantities indicated in the preceding paragraphs. This allows for any decomposition of the cyanuric halide, for example by hydrolysis to cyanuric acid, under the reaction conditions and gives a higher relative yield from the colouring matter which usually is more expensive than the other reactants. Usually up to 30% by weight in excess of cyanuric halide is sufficient, and frequently much less than this excess can be used.

The new colouring matters containing an azo group may also be obtained by coupling a diazonium compound with an azoic coupling component, where either the diazonium compound, or the coupling component, or both the diazonium compound and the coupling component, contain at least one s-triazinylamino group wherein at least one of the carbon atoms of the triazine nucleus is substituted by a negatively-substituted aryloxy group or by a substituted or unsubstituted arylthio group. In this modified process, it is preferable to carry out the diazotisation and coupling at as low a temperature as possible, preferably below 10° C. and to carry out the coupling at as low a pH as possible in order to avoid, so far as be possible, the replacement of negatively-substituted aryloxy or substituted or unsubstituted arylthio by hydroxy, which replacement occurs readily in strongly alkaline media.

The new colouring matters are valuable for the colouration of cellulosic textile materials, especially when the colouration is carried out in conjunction with an alkaline agent. This colouration process forms yet a further feature of the invention.

The treatment of the cellulosic textile material with the alkaline agent may be carried out prior to or during the treatment with the colouring matter, but it is preferred, in general, to treat the textile material with the alkaline agent after treating with the new colouring matter.

Suitable alkaline agents for use in the colouration process include, for example, caustic soda, caustic potash, sodium carbonate, sodium bicarbonate and trisodium phosphate.

When the whole surface of the textile material is to be coloured, the new colouring matter may be applied by immersing the textile material in an aqueous solution containing the new colouring matter and localised treatment with the new colouring matter may be carried out by printing with a printing paste containing the new colouring matter.

When the alkaline agent is applied simultaneously with the new colouring matter it may conveniently be dissolved in the aqueous solution or the printing paste containing the new colouring matter.

The aqueous solution of the new colouring matter, whether alkaline agent is present or not, may contain commonly used adjuvants to aqueous baths for the application of dyestuffs for example sodium chloride, sodium sulphate, sodium alginate, urea and water-soluble alkyl ethers of cellulose.

The printing paste, whether alkaline agent is present or not, may contain commonly used adjuvants for example urea, and thickening agents for example methyl cellulose, starch and locust bean gum, but it is preferred to use, as thickening agent, an alginate for example sodium alginate.

When the textile material has been treated with both the new colouring matter and the alkaline agent it may be washed, for example by rinsing in water, to remove loosely-bound colouring matter. In general, it is preferred to include, in the washing step, a scour with a hot dilute aqueous solution of soap or a detergent, since the colouring matter which is not removed by such a treatment is very fast to subsequent washing treatments.

In many cases it is found that the amount of colouring matter removed by such a scouring step is lessened if the coloured textile material is steamed for a short time, for example from one to five minutes, after it has been treated with both the new colouring matter and the alkaline agent.

When the new colouring matter used in the colouration process is colourless, it is to be understood that the colouration process includes any further treatments necessary to convert the colourless compound into a coloured compound. Such treatments may also, if desired, be included in the colouration process where the new colouring matter used in the colouration process is itself coloured but contains groups which, by after-treatment by known general methods, are known to enable the shade or fastness properties of coloured compounds to be altered.

Thus, when the new colouring matter is substituted by the appropriate groupings, it may be subjected on the fibre, for example to a diazotisation step followed by a a treatment with an azoic coupling component, to a treatment with a diazonium compound, or to a metallisation treatment.

When the new colouring matter is treated in situ on the fibre to change its shade or fastness properties, this treatment is preferably carried out after the textile material has also been treated with the alkaline agent, steamed and washed.

The invention is illustrated but not limited by the following examples in which parts are by weight:

Example 1

Diazotised 2-naphthylamine-4:8-disulphonic acid is coupled with m-toluidine and 41.9 parts of the disodium salt of the aminoazo compound so obtained are dissolved in 700 parts of water.

18.6 parts of cyanuric chloride are dissolved in 120 parts of acetone and the solution is added to a stirred mixture of 320 parts of ice and 240 parts of water. A solution containing 34.8 parts of phenol-4-sulphonic acid and 16 parts of caustic soda in 320 parts of water is added and the mixture is stirred until a clear solution of the disodium salt of 2:4-di(4'-sulphophenoxy)-6-chloro-s-triazine is obtained.

The solution of aminoazo compound is then added and the mixture is stirred and heated to 60° C. during 45 minutes. The mixture is neutralised to litmus by adding 10% aqueous sodium carbonate solution and then stirred, adding more sodium carbonate solution as necessary to keep it neutral, until all the aminoazo compound has reacted. (The presence of aminoazo compound may be detected by treating a portion of the reaction medium with dilute aqueous hydrochloric acid, when a pink colouration is obtained.)

The mixture is then cooled to 15° C. and acetone is added until a precipitate is formed. This precipitate is filtered off and dried at 30° C.

The dyestuff so obtained may be used to colour cellulosic textile materials such as cotton fabric by a number of methods of which the following are illustrative:

METHOD A

Cotton fabric is padded in a 2% aqueous solution of the dyestuff, then dried and padded in an aqueous solution containing 0.5% of caustic soda and 30% of sodium chloride. The fabric is steamed for 1 minute, rinsed in water, boiled in dilute soap solution for 5 minutes, rinsed again in water and dried. The fabric is coloured a yellow shade very fast to washing and to light.

METHOD B

A printing paste is made by mixing together 3 parts of the above product, 5 parts of urea, 51 parts of water, 40 parts of 5% aqueous sodium alginate solution and 1 part of sodium bicarbonate.

The printing paste is applied to cotton fabric by a silk screen printing technique. The fabric is dried and steamed at atmospheric pressure for 10 minutes. The print is then rinsed in cold water, boiled in dilute soap solution for 5 minutes, rinsed and dried.

The yellow print so obtained is fast to washing.

Example 2

Diazotised 3-aminoacetanilide-4-sulphonic acid is coupled with 1-(2':5'-dichloro-4-sulphophenyl)-3-methyl-5-pyrazolone, and the product obtained is boiled with dilute hydrochloric acid to convert the acetylamino group to an amino group.

53.8 parts of the disodium salt of the aminoazo compound so obtained are dissolved in 600 parts of water and added to a solution of the disodium salt of 2:4-di(4'sulphophenoxy)-6-chloro-s-triazine obtained as described in Example 1.

The mixture is stirred at between 0° and 10° C. for 12 hours and then at 40° C. for 12 hours, adding 10% aqueous sodium carbonate solution as necessary to make and keep the mixture neutral to litmus. The mixture is then cooled to 15° C. and 360 parts of salt are added. The product which separates is filtered off, washed with acetone and dried.

The dyestuff so obtained is found by analysis to contain 3.8 sulphur atoms for each azo group present. It

consists substantially of the 2:4-di(sulphophenoxy)-s-triazinyl derivative of the aminoazo compound used as starting material.

When applied by the methods described in Example 1, the dyestuff so obtained colours cellulosic textile materials in bright greenish yellow shades fast to washing and to light.

Example 3

A solution of the disodium salt of 2:4-di-(4'-sulphophenoxy)-6-chloro-s-triazine obtained as described in Example 1 from 4.61 parts of cyanuric chloride is stirred at 20° C. and a solution of 13.3 parts of the disodium salt of 1-amino-4-(4'-aminoanilino)anthraquinone-2:3'-disulphonic acid in 250 parts of water is added during 20 minutes. The mixture is then heated to 50° C. and stirred at 48° C. to 50° C. for 2½ hours during which time the mixture is kept neutral to litmus by the gradual addition of 10% sodium carbonate solution. The mixture is then cooled to 25° C., a solution of 4 parts of anhydrous disodium hydrogen phosphate and 8 parts of anhydrous potassium dihydrogen phosphate in 40 parts of water is added and then sufficient sodium chloride to give a concentration of 240 grm. per litre is added. The mixture is stirred until precipitation of the dyestuff is complete, then filtered and the dyestuff washed on the filter with a solution of 48 parts of sodium chloride, 3 parts of anhydrous disodium hydrogen phosphate and 6 parts of anhydrous potassium dihydrogen phosphate in 200 parts of water and is finally dried at room-temperature.

The dyestuff so obtained when applied to cotton fabric by the methods described in Example 1 gives blue shades of good fastness to washing and to light. It is found by analysis to contain practically no hydrolysable chlorine and it has a nitrogen to sulphur ratio of 6:3.8. The theoretical nitrogen to sulphur ratio of the di-(sulphophenoxy)-triazinyl derivative of the aminoanthraquinone compound used as starting material is 6 to 4.

Example 4

20 parts of copper phthalocyanine-4-N-(3'-amino-4'-sulphophenyl)-sulphonamide-4-sulphonic acid (obtained as described below) are dissolved in 700 parts of water and sufficient 2 N aqueous sodium carbonate solution is added to give a solution of pH 7. 20 parts of the potassium salt of 2-chloro-4:6-di-(2'-sulpho-4'-methylphenoxy)-s-triazine are added and the mixture is stirred at 80° C. the pH being adjusted to pH 7 at short intervals by addition of 10% aqueous sodium carbonate solution until the reaction is complete. 200 parts of sodium chloride are then added and the precipitated dyestuff is filtered off, washed with saturated brine and dried.

When applied to cotton by the methods described in Example 1, the product gives greenish blue dyeings of good fastness to washing.

The potassium salt of 2-chloro-4:6-di-(2'-sulpho-4'-methylphenoxy)-s-triazine used in the above example is obtained by adding a solution of 37.2 parts of cyanuric chloride in 160 parts of acetone to a solution of 90 parts of the potassium salt of 2-sulpho-4-methylphenol in 1200 parts of water at 0–5° C. A solution of 22.4 parts of potassium hydroxide in 1000 parts of water is added slowly with stirring. The mixture is then heated to 25° C. for one hour. 400 parts of potassium chloride are added and the precipitated product is filtered off and dried.

The copper phthalocyanine-4-N-(3'-amino-4'-sulphophenyl)-sulphonamide-4-sulphonic acid used in the above example is obtained in the following manner: 448 parts of copper phthalocyaninetetra-4-sulphonic acid is heated with 4750 parts of chlorosulphonic acid at 115° C. to 120° C. for 4 hours. The resulting solution is cooled to 20° C. and drowned carefully into ice-water with stirring, maintaining the temperature below 2° C. by further additions of ice as required, and the suspension obtained is filtered at 0° C. The residue on the filter is washed with a little ice-water, pressed well to remove most of the mineral acid, suspended in 10,000 parts of ice-water, and the residual mineral acidity is removed by addition of sodium carbonate. 336 parts of sodium bicarbonate are then added, followed by a neutral solution prepared by dissolving 284 parts of 2:4-diaminobenzenesulphonic acid in 2000 parts of water containing 156 parts of sodium bicarbonate and the mixture is stirred for 16 hours, allowing the temperature to rise to 20° C. to 25° C. The resulting blue suspension is acidified by addition of 360 parts of 38% aqueous hydrochloric acid, the precipitate is filtered off, washed well with 2 N aqueous hydrochloric acid and dried.

Example 5

20 parts of copper phthalocyanine-4-N-(3'-amino-4'-sulphophenyl)-sulphonamide-4-sulphonic acid (obtained as described in Example 4) are dissolved in 700 parts of water and sufficient 2 N aqueous sodium carbonate solution is added to give a solution of pH 7. 18 parts of the sodium salt of 2-chloro-4:6-di-(2'-nitro-4'-sulphophenoxy)-s-triazine (obtained as described below) are added, and the mixture is stirred at from 60 to 70° C., the pH being adjusted to pH 7 at short intervals by addition of 2 N aqueous sodium carbonate solution until the reaction is complete. 200 parts of sodium chloride are then added and the precipitated dyestuff is filtered off, washed with saturated brine and dried.

When applied to cotton by the methods described in Example 1, the product gives bright blue dyeings of good fastness to washing.

The sodium salt of 2-chloro-4:6-di(2'-nitro-4'-sulphophenoxy)-s-triazine used in the above example is obtained by adding a solution of 27.9 parts of cyanuric chloride in 120 parts of acetone to a solution of 72.6 parts of the sodium salt of 2-nitro-4-sulphophenol in 1500 parts of water at between 0 and 5° C. A solution of 12 parts of sodium hydroxide in 200 parts of water is added slowly with stirring. The mixture is then heated to between 10 and 15° C. for one hour. 200 parts of sodium chloride are added and the precipitated product is filtered off and dried.

Example 6

4.6 parts of cyanuric chloride are dissolved in 30 parts of acetone and the solution is poured into a stirred mixture of 50 parts of ice and 100 parts of water at a temperature below 3° C. To the suspension so obtained there is added during 30 minutes at between 0 and 4° C. a solution of 11.0 parts of 2-nitrophenol-4-sulphonic acid and 4 parts of sodium hydroxide in 50 parts of water. The mixture is then stirred for one hour at this temperature and a solution of 9.1 parts of the disodium salt of the aminoazo compound used in Example 1 in 150 parts of water is added during 30 minutes at between 5 and 10° C. The mixture is heated to 20° C. and after 30 minutes the mixture is neutralised to pH 7 with dilute sodium carbonate solution. The reaction mixture is stirred for a further 16 hours at room temperature the solution being maintained at pH 7. There is then no free aminoazo compound present. 40 parts of sodium chloride are added and the dystuff which separates is filtered off and dried at room temperature.

The product so obtained has a nitrogen to sulphur ratio of 8 to 3.95. The theoretical nitrogen to sulphur ratio of the di(2'-nitro-4'-4-sulphophenoxy)-s-triazinyl derivative of the aminoazo compound used as starting material is 8 to 4.

When applied to cotton by the methods described in Example 1, the product gives yellow shades of good fastness to severe washing and fast to light.

Example 7

4.6 parts of cyanuric chloride are dissolved in 30 parts

of acetone and the solution is added to a stirred mixture of 50 parts of ice and 100 parts of water below 3° C. A suspension of 7.97 parts of 1-amino-8-hydroxynaphthalene-3:6-disulphonic acid in 40 parts of water is made neutral to litmus by the addition of sodium carbonate. The solution so obtained is added during 30 minutes at 3° C. to the suspension of cyanuric chloride. 15 minutes after the addition there is no free 1-amino-8-hydroxynaphthalene-3:6-disulphonic acid left in the mixture. The acidity which has developed is removed by adding dilute sodium carbonate solution. 4.32 parts of orthanilic acid are diazotised and added to the mixture at between 5 and 10° C., the solution being maintained at pH 7 by addition of sodium carbonate solution. The reaction mixture is stirred for 16 hours, then 30 parts of sodium chloride are added and the product which separates is filtered off, dissolved in 150 parts of water and a solution of 10.8 parts of sodium phenol-4-sulphonate and 2.2 parts of sodium hydroxide in 50 parts of water are added at room temperature. The mixture is stirred for 4 hours at 20° C. and for 16 hours at 40° C. Acetone is added and the dyestuff which precipitates is filtered off and dried at room temperature.

The dyestuff so obtained is found by analysis to contain 4.8 sulphur atoms for each azo group present. It consists substantially of the di(4-sulphophenoxy)triazinyl derivative of the aminoazo compound obtained from diazotised orthanilic acid and 1-amino-8-naphthol-3:6-disulphonic acid which theoretically contains 5 sulphur atoms for each azo group.

The dyestuff obtained when applied to cotton fabric by the methods described in Example 1 gives red shades of good fastness to washing and to light.

Example 8

A solution of 7.23 parts of sodium phenol-4-sulphonate and 1.47 parts of sodium hydroxide in 50 parts of water is added during 30 minutes below 5° C. to a solution in 300 parts of water of 10.07 parts of the sodium salt of the compound obtained by coupling the condensation product from equimolecular proportions of the sodium salt of 2-amino-5-hydroxy-naphthalene-7-sulphonic acid and cyanuric chloride with diazotised p-chloroaniline.

The mixture is stirred below 10° C. for 16 hours and at 40° C. for a further 12 hours. 35 parts of sodium chloride are added and the precipitated dyestuff is filtered off and dried at room temperature.

The dyestuff so obtained is found by analysis to contain 2.7 sulphur atoms for each azo group present. It consists substantially of the di(4-sulphophenoxy)triazinyl derivative of the aminoazo compound obtained from 2-amino-5-naphthol-7-sulphonic acid and diazotised p-chloroaniline which theoretically contains 3 sulphur atoms for each azo group.

The dyestuff when applied to cotton fabric by the methods described in Example 1 gives orange shades of good fastness to washing and to light.

Example 9

A solution of 6.13 parts of 2-nitrophenol-4-sulphonic acid and 2.24 parts of sodium hydroxide in 50 parts of water is added during 30 minutes at below 3° C. to a solution in 100 parts of water of 10 parts of the trisodium salt of the compound obtained by coupling the condensation product from equimolecular proportions of the disodium salt of 1-amino-8-hydroxynaphthalene-3:6-disulphonic acid and cyanuric chloride with diazotised orthanilic acid in the presence of sodium acetate. The solution is stirred for 16 hours at below 10° C. and for 24 hours at 40° C. The dyestuff is precipitated from solution by the addition of much acetone, filtered off and dried at room temperature.

The dyestuff so obtained is found by analysis to contain 4.6 sulphur atoms for each azo group present. It consists substantially of the di-(2-nitro-4-sulphophenoxy)triazinyl derivative of the aminoazo compound obtained from diazotised orthanilic acid and 1-amino-8-naphthol-3:6-disulphonic acid which theoretically contains 5 sulphur atoms for each azo group. When applied to cotton fabric by the methods described in Example 1 it gives red shades of good fastness to washing and to light.

Example 10

A solution of 6.5 parts of sodium-2-chlorophenol-4-sulphonate and 1.12 parts of sodium hydroxide in 50 parts of water is added during 30 minutes at below 3° C. to a solution in 100 parts of water of 10 parts of the trisodium salt of the compound obtained by treating the condensation product from the disodium salt of 1-amino-8-hydroxynaphthalene-3:6-disulphonic acid and one equivalent of cyanuric chloride with diazotised orthanilic acid in the presence of sodium acetate. The mixture is stirred for 16 hours at below 10° C. and for 24 hours at 40° C. The dyestuff is precipitated from solution by the addition of much acetone, filtered off and dried at room temperature.

The dyestuff so obtained is found to contain 4.7 sulphur atoms for each azo group present. It consists substantially of the di(2-chloro-4-sulphophenoxy)triazinyl derivative of the aminoazo compound obtained from diazotised orthanilic acid and 1-amino-8-naphthol-3:6-disulphonic acid, which theoretically contains 5 sulphur atoms for each azo group present. When applied to cotton fabric by the methods described in Example 1 it gives red shades of good fastness to washing and to light.

Example 11

A solution of the disodium salt of 2:4-di(4'-sulphophenoxy)-6-chloro-s-triazine is obtained as described in Example 1 and there is added a solution of 19.96 parts of the sodium salt of 1:3-phenylenediamine-4-sulphonic acid in 100 parts of water during 15 minutes at 5° C. The mixture is stirred for 16 hours at between 5 and 10° C., the acidity which develops being neutralised by addition of dilute sodium carbonate solution.

The solution is then cooled to below 5° C., and 40 parts of concentrated hydrochloric acid are added. 52 parts of 2 N sodium nitrite solution are added and then excess nitrous acid is removed by adding sulphamic acid.

The diazo solution so formed is added to a well stirred solution of 23.68 parts of 2:3-hydroxynaphthoic anilide in 800 parts of water and 160 parts of 2 N sodium hydroxide solution at between 0 and 5° C. during 30 minutes; 300 parts of sodium acetate crystals are added and the mixture is stirred for 16 hours at below 10° C. 440 parts of sodium chloride are then added and the dyestuff which precipitates is filtered off and dried at room temperature.

The dyestuff so obtained contains 3.1 atoms of sulphur for each azo group present. It consists substantially of the di-(4-sulphophenoxy)triazinyl derivative of 1-(3'-amino 4'-sulphophenylazo)-2-hydroxy-3-naphthoic anilide which theoretically contains 3 sulphur atoms for each azo group present. When applied to cotton fabric by the methods described in Example 1 it gives red shades of good fastness to washing and to light.

Example 12

To a solution of the disodium salt of 2:4-di(4'-sulphophenoxy)-6-chloro-s-triazine obtained as described in Example 1, there is added a solution of 26.4 parts of 2:3-hydroxynaphthoic-3'-aminoanilide in 600 parts of acetone and 200 parts of water during 15 minutes at 5° C. The mixture is stirred at 20° C. for 16 hours and then at 35° C. for 4 hours, the acidity which develops being neutralised to pH 7 by adding sodium carbonate solution. There is then added a solution of the diazonium compound obtained from 16.44 parts of orthanilic acid.

The mixture is stirred for 16 hours at below 10° C.,

and the precipitate is filtered off and dried at room temperature.

The dyestuff so obtained is found to contain 2.8 atoms of sulphur for each azo group present. It consists substantially of the di(4'-sulphophenoxy)triazinyl derivative of 1-(2'-sulphophenylazo)-2-hydroxy-3 - naphthoic - (3''-amino)anilide which theoretically contains 3 sulphur atoms for each azo group. When applied to cotton fabric by the methods described in Example 1 it gives red shades of good fastness to washing and to light.

Example 13

A solution of the disodium salt of 2:4-di(4'-sulphophenoxy)-6-chloro-s-triazine obtained as described in Example 1 is condensed with 1 molecular proportion of p-phenylene diamine and the product obtained is diazotised using the methods described in the first two paragraphs of Example 11.

The diazonium compound so obtained is then coupled with the coupling component used in Example 12 in the presence of sodium acetate, the dyestuff being precipitated by adding ethanol to the reaction mixture.

The dyestuff so obtained is found to contain 3.65 atoms of sulphur for each azo group present. It consists substantially of the bis-[di-(4'-sulphophenoxy)triazinyl] derivative of 1-(4'-aminophenylazo)-2-hydroxy-3-naphthoic-(3''-amino)anilide, which theoretically contains 4 sulphur atoms for each azo group. When applied to cotton fabric by the methods described in Example 1, it gives violet shades of good fastness to washing and to light.

Example 14

18.6 parts of cyanuric chloride are dissolved in 120 parts of acetone and the solution is added to a stirred mixture of 400 parts of water and 400 parts of ice below 3° C. To the suspension so formed there is added during 30 minutes, at between 0 and 4° C., a solution of 42.4 parts of thiophenol-4-sulphonic acid and 16 parts of sodium hydroxide in 200 parts of water, and the reaction mixture is then stirred for a further 30 minutes.

37.4 parts of the disodium salt of the aminoazo compound used in Example 1 are dissolved in 600 parts of water and this solution is then added to the mixture during 30 minutes. The mixture is stirred for 16 hours at below 10° C., then neutralized to litmus by adding 10% sodium carbonate solution heated to 20° C. and stirred, adding more sodium carbonate solution as necessary to keep it neutral, until all the aminoazo compound has reacted, as shown by the test described in Example 1.

180 parts of sodium chloride are then added and the precipitated dyestuff is filtered off and dried at room temperature.

The dyestuff so obtained is found by analysis to contain 6 sulphur atoms for each azo group present, and consists substantially of the 2:4-di(4-sulphophenylthio)-s-triazinyl derivative of the aminoazo compound used as starting material.

Example 15

A solution of 18.5 parts of cyanuric chloride in 100 parts of acetone is poured into a stirred mixture of 280 parts of water and 280 parts of crushed ice and to the suspension formed there is added during 30 minutes a solution containing 34.8 parts of phenol-3-sulphonic acid and 8 parts of caustic soda in 320 parts of water keeping the temperature of the mixture below 5° C. throughout.

To the clear solution obtained there is added a solution containing 48.0 parts of the disodium salt of 1-amino-4(4'-aminoanilino)anthraquinone-2:3'-disulphonic acid in 700 parts of water and the mixture is heated during 45 minutes to 80° C. and stirred at between 80 and 85° C. for 1½ hours. The solution is then cooled to 20° C. and the product is salted out by addition of sodium chloride filtered off and dried at 50° C.

When applied to cotton fabric by Method A of Example 1 the fabric is coloured a blue shade very fast to washing and to light.

Example 16

If in Example 15 the 34.8 parts of phenol-3-sulphonic acid are replaced by 27.6 parts of phenol-3-carboxylic acid a blue dyestuffff having similar properties is obtained.

Example 17

15 parts of copper phthalocyanine-4-N-(3'-amino-4'-sulphophenyl)-sulphonamide-4-sulphonic acid (obtained as described in Example 4) are dissolved in 700 parts of water and sufficient 2 N aqueous sodium carbonate solution is added to give a solution of pH 7. The solution is stirred and cooled to 5° C. and a solution of 4 parts of cyanuric chloride in 70 parts of acetone is added. The pH of the mixture is brought to 7 by adding 2 N aqueous sodium carbonate solution. When the reaction is finished, a solution of 7.3 parts of sodium thiophenol-3-sulphonate and 1.4 parts of sodium hydroxide in 200 parts of water is added. The mixture is heated to 45° C. for 2½ hours then 300 parts of potassium chloride are added and the precipitated dyestuff is filtered off, washed with saturated potassium chloride solution and dried.

The product so obtained colours cellulosic materials in greenish-blue shades of good wash-fastness when applied by the methods described above.

Similar products are obtained if the sodium thiophenol-3-sulphonate used in the above example is replaced by 9.1 parts of sodium 2-thionaphthol-6-sulphonate or by 12.6 parts of disodium-2-thionaphthol-6:8-disulphonate.

Example 18

The process described in Example 17 is repeated except that the sodium thiophenol-3-sulphonate is replaced by 5.0 parts of 4-chlorothiophenol. A similar product is obtained.

Example 19

8.7 parts of 2:4-dinitro-4'-aminodiphenylamine-3'-sulphonic acid (obtained by the condensation of 2:4-dinitrochlorobenzene with p-phenylenediamine-sulphonic acid in aqueous ethanol solution in presence of calcium carbonate) are dissolved in 250 parts of water. A solution of 16 parts of the potassium salt of 2-chloro-4:6-di(2'-sulpho-4'-methylphenoxy)-s-triazine obtained as described in Example 4, in 150 parts of water is added. and the reaction mixture is heated at from 95 to 100° C. The pH of the solution is adjusted to 7 at short intervals by the addition of 2 N sodium carbonate solution, until the reaction is complete. The hot solution is filtered, 80 parts of sodium chloride are added and the mixture is cooled. The supernatant liquor is decanted from the tarry product, and the latter is dried in vacuo at 25° C.

When applied to cotton by the methods described in Example 1, brownish-yellow dyeings are obtained.

Example 20

A solution of 9.25 parts of cyanuric chloride in 60 parts of acetone is added to a stirred mixture of 100 parts of water and 80 parts of ice. A solution of 26.65 parts of the disodium salt of 1-amino-4-(3'-aminoanilino)anthraquinone-2:4'-disulphonic acid in 300 parts of water is added during 45 minutes. The mixture is then stirred for 1 hour at between 0 and 5° C. and is then made neutral to litmus by the gradual addition of 2 N sodium carbonate solution.

A solution of 8 parts of sodium hydroxide and 13.8 parts of 4-hydroxybenzoic acid in 200 parts of water is added during 30 minutes, the temperature being allowed to rise to 20° C. The mixture is then heated to 50° C. and stirred at 50° C. for 1 hour, and then at 60° C. for 18 hours. The dyestuff is precipitated from solution by the addition of much acetone, filtered off and dried.

The dyestuff so obtained is found by analysis to contain practically no hydrolyseable chlorine and when

applied to cotton fabric by the methods described in Example 1 gives blue shades of good fastness to washing and light.

Example 21

400 parts of acetone are added to a solution of the disodium salt of 2:4-di(4'-sulphophenoxy)-6-chloro-s-triazine obtained as described in Example 1. A solution of 25.0 parts of 2:3-hydroxynaphthoic-3'-aminoanilide in 300 parts of acetone is then added during 15 minutes at 5° C. The acidity which develops is neutralised to pH 7 by adding sodium carbonate solution. The mixture is heated to 40° C. and the acetone allowed to evaporate; after 3 hours there is no trace of unreacted amino compound. The clear solution obtained is cooled to 10° C. and a solution of the tetrazonium salt obtained from 11.0 parts of 3:3'-di-methoxy-4:4'-diaminodiphenyl in the normal manner is added at 10° C. Mineral acidity is removed by the addition of sodium acetate solution. When the coupling is complete the dye is precipitated from solution by the addition of much alcohol, filtered off and dried at 40° C.

When applied to cotton fabric by the method of Example 1 the fabric is coloured a blue shade fast to washing.

Example 22

If, in Example 6 the 11.0 parts of 2-nitrophenol-4-sulphonic acid and 4 parts of sodium hydroxide are replaced by 12.7 parts of phenol-2:5-disulphonic acid and 6 parts of sodium hydroxide respectively a yellow dyestuff having similar properties is obtained.

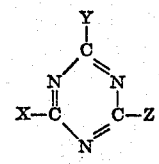
Example 23

18.6 parts of cyanuric chloride are dissolved in 120 parts of acetone and the solution is added to a stirred mixture of 320 parts of ice and 240 parts of water. A solution containing 50.8 parts of phenol-2:4-disulphonic acid and 24 parts of sodium hydroxide in 320 parts of water is added at 50° C. and stirred until a clear solution of the tetrasodium salt of 2:4-di(2':4'-disulphophenoxy)-6-chloro-s-triazine is obtained. 50 parts of Cellosolve are then added followed by a solution of 22.2 parts of 2:3-hydroxynaphthoic-3'-aminoanilide in 400 parts of Cellosolve during 30 minutes. The mixture is heated to 40° C. and stirred until all the amino compound has reacted, sodium carbonate solution being added to keep the pH at 7. The solution is cooled to 5° C. and then a solution of the diazonium compound from 24 parts of 4-benzoylamino-2:5-diethoxyaniline is added during 15 minutes, sodium carbonate being added to maintain pH 8.4. When the coupling is complete the dye is precipitated from solution by the addition of much acetone, filtered off and dried at 40° C.

The dyestuff so obtained is found by analysis to contain 4.1 sulphur atoms for each azo group present. It consists substantially of the 2:4-di(2':4'-disulphophenoxy)-s-triazinyl derivative of the aminoazo compound obtained from diazotised 4-benzoylamino-2:5-diethoxyaniline and 2:3-hydroxynaphthoic-3'-aminoanilide which theoretically contains 4 sulphur atoms for each azo group present. When applied to cotton fabric by the methods described in Example 1 it gives blue shades of moderate fastness to washing.

What we claim is:

1. Process for coloring cellulose textile materials which comprises impregnating said textile materials in aqueous medium with a water-soluble coloring matter having the formula



wherein X stands for a chromophoric group containing a nitrogen atom, said chromophoric group being attached to the triazine ring through said chromophoric nitrogen atom; Y is a radical selected from the group consisting of mono- and di-cyclic aryloxy substituted by at least one member selected from the group consisting of chloro, sulfo, carboxy, and nitro, and mono- and di-cyclic and arylthio groups substituted in turn by at least one member selected from the group consisting of hydrogen, methyl, chloro, sulfo, carboxy, and nitro;

Z is a radical selected from the group consisting of Y and members of the class consisting of methyl, methylamino, propylamino, isopropylamino, butylamino, cyclohexylamino, dimethylamino, diethylamino, β-chloroethylamino, β-hydroxyethylamino, β-carboxyethylamino, β-sulfoethylamino, β-sulfatoethylamino, gamma-chloro-β-hydroxypropylamino, methoxy, ethoxy, β-chloroethoxyphenyl, anilino, chloroanilino, and N-methylanilino; and subjecting said cellulose textile materials to the action of an alkaline agent in aqueous medium so that said coloring reacts chemically with said cellulose textile material.

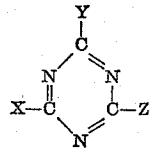
2. The process of claim 1, wherein said cellulose textile materials are first treated with said alkaline agent, and thereafter impregnating with said water-soluble coloring matter.

3. The process of claim 1, wherein said cellulose textile materials are treated with said alkaline agent during said impregnation with said water-soluble coloring matter.

4. The process of claim 1, wherein said cellulose textile materials are first impregnated with said water-soluble coloring matter and thereafter treated with said alkaline agent.

5. The process of claim 1, for the printing of cellulose textile materials wherein said water-soluble coloring matter and said alkaline agent are applied simultaneously to said cellulose textile materials in a printing paste.

6. Water-soluble coloring matters having the formula



wherein X stands for a chromophoric group containing a nitrogen atom, said chromophoric group being attached to the triazine ring through said chromophoric nitrogen atom;

Y is a radical selected from the group consisting of mono- and di-cyclic aryloxy substituted by at least one member selected from the group consisting of chloro, sulfo, carboxy, and nitro, and mono- and di-cyclic and arylthio groups substituted in turn by at least one member selected from the group consisting of hydrogen, methyl, chloro, sulfo, carboxy, and nitro;

Z is a radical selected from the group consisting of Y and members of the class consisting of methyl, methylamino, propylamino, isopropylamino, butylamino, cyclohexylamino, dimethylamino, diethylamino, β-chloroethylamino, β-hydroxyethylamino, β-carboxyethylamino, β-sulfoethylamino, β-sulfatoethylamino, gamma-chloro-β-hydroxypropylamino, methoxy, ethoxy, β-chloroethoxyphenyl, anilino, chloroanilino, and N-methylanilino.

7. The water-soluble coloring matters of claim 6, wherein said radical Z is the same as said radical Y.

8. 2:4-di-(4'-sulfophenoxy)-6-(p-[4'':8'' - disulfo - 2''-naphthylazo]-m-methylanilino)-s-triazine.

9. 2:4-di-(2'-sulfo-4'-methylphenoxy) - 6 - (2''-sulfo-5''-[4'''-sulfo-copper phthalocyanine-4''' - sulfonamido]-anilino)-s-triazine.

10. 2:4-di-(4 - sulfophenylthio)-6-(p-[4'':8'' - disulfo-2''-naphthylazo]-m-methylanilino)-s-triazine.

11. 2:4-di-(6':8'-disulfo-2'-naphthylthio-6-(2'' - sulfo-5''-[4'''-sulfo-copper phthalocyanine-4''' - sulfonamido]-anilino)-s-triazine.

12. 2:4-di-(4'-chlorophenylthio)-6 - (2''-sulfo - 5''-[4'''-sulfo-copper phthalocyanine - 4''' - sulfonamido]-anilino)-s-triazine.

13. 2:4-di-(4'-carboxyphenoxy) - 6 - (3'' - [1''' - amino-2'''-sulfo-anthraquinone-4'''-amino] - 6'' - sulfo-anilino)-s-triazine.

14. 2:4-di-(2':4' - disulfophenoxy) - 6 - (3''-[1''':2^{iv}:5^{iv}-diethoxy-4^{iv}-benzoylaminophenylazo - 2'''-hydroxy - 3'''-naphthoylamino]-anilino)-s-triazine.

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