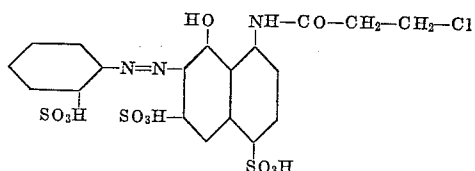


Table I—Continued

No.	Dyestuff	Shade on cellulose fibres
2		Blue.
3		Violet.
4		Brilliant red.

EXAMPLE 2

Mercedised cotton is foularded with an aqueous solution which contains, 1000 parts, 20 of the dyestuff of the formula



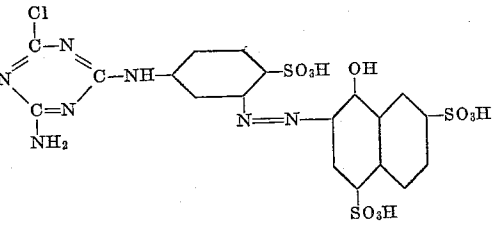
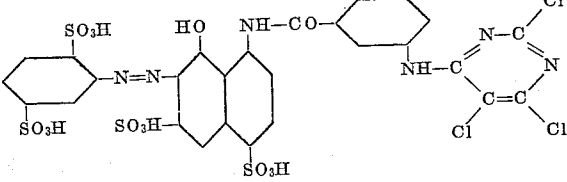
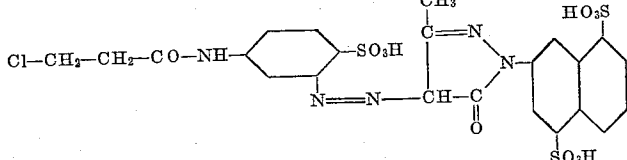
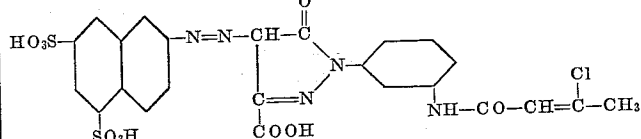
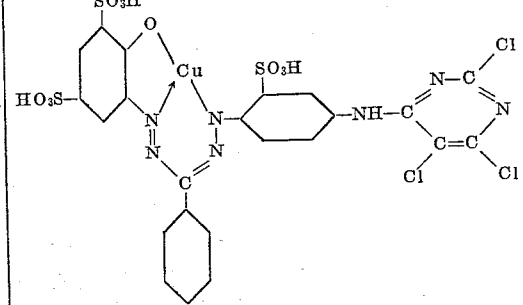
75 parts of urea, 20 parts of sodium metasilicate and 5 parts of sodium hydroxide solution 36° Bé. The impregnated material is then dried at 70° in a Lyonair dryer to a moisture of 8% and subjected to a heat treatment with 220° hot air for half a minute. The goods so treated are rinsed hot, soaped at the boil for 30 minutes, again rinsed and dried. A strong, vivid, wet-fast, scarlet dyeing is obtained.

If the fixing is performed without sodium hydroxide but otherwise in the same way, then a considerably more weak dyeing is obtained.

On the other hand, an equally good result is obtained if, instead of the sodium hydroxide solution, corresponding amounts of potassium hydroxide solution are used.

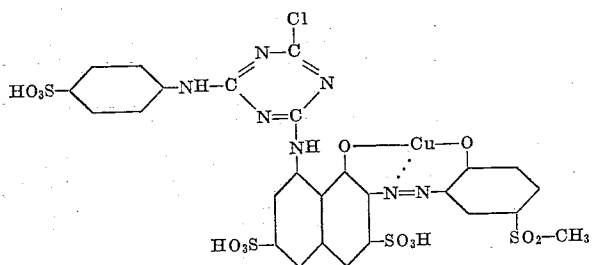
If, in the process described above, the dyestuffs given in the following Table II are used under otherwise the same conditions, then deep, brilliant, wet-fast dyeings are obtained.

Table II

No.	Dyestuff	Shade on cellulose fibres
1.....		Scarlet:
2.....		Brilliant red.
3.....		Yellow.
4.....		Reddish yellow.
5.....	<p>Condensation product from 1 mol of copper phthalocyanine disulphonic acid disulphochloride and 1 mol of ammonia, 1 mol 2,4-diaminobenzene-1-sulphonic acid and 1 mol of 2,4,5,6-tetrachloropyrimidine.</p>	Turquoise blue.
6.....		Blue.

EXAMPLE 3

Cotton is printed by one of the usual methods with the following printing paste:
40 parts of the dyestuff of the formula



85 parts of urea
215 parts of water
638 parts of 5% aqueous sodium alginate
20 parts of sodium carbonate
2 parts of sodium hydroxide solution 36° Bé.

1000 parts printing paste

The printed textile goods are dried in a lyonnair dryer at 65° to a moisture of 10% and then the print is fixed for 1 minute at 180° over a drum dryer. The goods so treated are rinsed first cold and then hot, then soaped at the boil for 30 minutes with a solution of 2 parts of curd soap in 1000 parts of water, again rinsed and dried. A deep, pure, wet-fast violet print is obtained. A much weaker print is obtained with otherwise the same process but without the use of sodium hydroxide solution in the printing paste.

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3,143,390

PROCESS FOR THE DYEING AND PRINTING OF CELLULOSE FIBRES

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 No Drawing. Filed Sept. 21, 1962, Ser. No. 225,384
 Claims priority, application Switzerland Sept. 22, 1961
 1 Claim. (Cl. 8-54.2)

The present invention concerns a process for the dyeing and printing of cellulose fibres with reactive dyestuffs and the material so fast dyed or printed thereby.

It is known that cellulose fibres can be impregnated with dye liquors or printing pastes containing reactive dyestuffs in the presence of salts having a basic reaction and easily soluble carbamides, subjected to a heat treatment at 100-150° for 4-10 minutes and then rinsed and soaped. The impregnation of cellulose material at a low temperature with liquors or printing colours containing reactive dyestuffs, stronger alkalies than trisodium phosphate and, possibly, easily soluble carbamides, leaving of the impregnated goods in a damp condition for several hours at room temperature to fix the dyestuffs and finally rinsing and soaping is also known. In addition it is known that the caustic alkalies preferably used in the warm fixing processes usual up to the present lead to unacceptable losses in colour and clouding of the shades.

It has now been found that reactive dyestuffs can be fixed onto cellulose material surprisingly in a shorter time than is possible with the shortest known process, free from any of the above drawbacks by impregnating the material to be dyed or printed with possibly thickened liquors which, in addition to the usual amounts of reactive dyestuffs, contain easily soluble carbamides and, possibly, salts having a basic reaction, and caustic alkalies, heating the impregnated and dried material containing at least 5 to 8% but not more than 25% and preferably maximally 15% of moisture for a short time, namely only ½ to 2 minutes at the unconventionally high temperatures of at least 170° C., then rinsing, soaping, again rinsing and drying. At lower temperatures losses of time and/or insufficient fixation are unavoidable.

It is one important advantage of this process according to the invention that the amounts of easily water soluble carbamides can be reduced to 50 to maximally 95 grams, and preferably 75 to 90 grams, per kilogram of solution or paste. The impregnating liquors or printing colours usable according to the invention contain, for example, lithium, sodium or potassium hydroxide as caustic alkalies. They can contain as "basically reacting salts" which is used hereinafter in the specification and the appended claims sodium or potassium carbonate, disodium or trisodium phosphate, tetrasodium pyrophosphate or alkali-metal metasilicate. The term "easily water soluble carbamides" as used in this specification and the appended claims, describing the agents usable according to the invention in the impregnation liquors and printing colours which promote swelling of the fibre are urea, thiourea, acetamide, guanidine and the easily water soluble salts thereof, especially guanidine carbonate.

To attain light to medium dyeings or prints according

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to the present process preferably, about 2 to 20 g. of reactive dyestuff, 0 to 0.15 mole of basically reacting salts, 0.01 to 0.15 mole of caustic alkali and 50 to 150 g. of easily water soluble carbamide are used per kilogram of dyeing liquor or printing paste. For medium to deep shades, 20 to 80 g. reactive dyestuff, 0.15 to 0.3 mole basically reacting salts, 0.1 to 0.3 mole caustic alkali and the aforesaid amount of easily water soluble carbamide are used per kilogram of dyeing liquor or printing paste.

The cellulose fibres impregnated with dyeing liquors or printing pastes containing reactive dyestuff, basically reacting salt, caustic alkali and easily water soluble carbamide are treated, according to the present process to fix the reactive dyestuff, preferably for ½ to 2 minutes at 170-220° with either inert gases, steam or contact heaters.

The reactive dyestuffs with which fast and deep dyeings and prints are attained with a short fixing time and high temperature on cellulose fibres such as cotton, viscose rayon, staple fibre, ramie and hemp according to the invention, can be of various dyestuff classes; they can be, for example, azo, anthraquinone, phthalocyanine or formazyl dyestuffs which, in particular, can also contain heavy metal of the atomic numbers 24-29 in first line copper or chromium bound in complex linkage.

The reactive groups of these dyestuffs contain at least one substituent which, under the fixing conditions, splits off as anion. The reactive group consists, for example, of the radical of a cyclic carbimide halide which contains at least one mobile halogen atom bound to a carbon atom in the ring which is adjacent to a tertiary ring nitrogen atom. The reactive group can consist, in particular, of an azine ring of aromatic character which contains at least two tertiary ring nitrogen atoms and at least one mobile halogen atom bound to ring carbon adjacent to such nitrogen atoms such as, e.g. chlorine or bromine; examples of such reactive group are a mono-, di- or tri-halogen diazinyll or a mono- or di-halogen triazinyll group. Furthermore, the dyestuffs usable according to the invention may contain, as reactive groups, β -chloro or β -bromo fatty acid amide groups especially β -chloro-crotonic acid amide or β -chloro propionic acid amine groups.

Finally, also an alkylsulphonyl or a sulphonic acid-N-alkylamide group can be present as reactive grouping, which group contains a sulphonyloxy group or a halogen atom at a β -carbon atom of the aliphatic chain; such substituents are, e.g. the sulphated β -hydroxyethylsulphonyl and the sulphated sulphonic acid-N- β -hydroxyethylamide group as well as the sulphonic acid-N- β -chloro- or sulphonic acid-N- β -bromoethylamide groups.

Preferably however, the reactive grouping is a radical which only forms a chemical bond with hydroxyl or alcoholate groups while splitting off, as anion under sharper conditions. The substituents so defined in the specification and in the claims are, the mono-chloro-s-triazinyll, dichloro-m-diazinyll or trichloro-m-diazinyll radical, the β -chloropropiononyll or the β -chlorocrotononyll. Very valuable reactive dyestuffs are these, which contain a polyhalogenopyrimidylamino group especially a di- or trichloropyrimidylamino group.

Cellulose fibres are dyed or printed in general by the usual methods with impregnating liquors or printing colours usable according to the invention which contain alkali hydroxide.

The dye liquors or printing pastes which, per kilogram, contain 2 to 80 g. of reactive dyestuff, 50 to 200 g. of easily water soluble carbamide, particularly urea, and 0 to 0.3 mole of salt having a basic reaction, are mixed advantageously immediately before use with 0.01 to 0.3 mole of caustic alkali. After the dyeing or printing, the fibres are advantageously dried at mild temperatures of 50 to 90° C. and then treated for ½ to 2 minutes with 170–220° hot, inert gases or steams such as hot air or superheated steam or with 170–220° hot contact heaters. The dyed or printed fibres are finished by one of the methods usual for reactive dyestuffs by rinsing, soaping, again rinsing and drying.

A modification of the process consists in first impregnating or printing the cellulose fibres with a dye liquor or printing paste which contains, per kilogram, 2 to 80 g. of reactive dyestuff, 50 to 200 g. of easily water soluble carbamide and 0 to 0.8 mole of basically reacting salts, if desired, drying the treated goods, then pad dyeing with a solution which contains 200 to 400 parts and preferably 300 parts of a neutrally reacting electrolyte, e.g. sodium chloride and 0.01 to 0.3 mole of caustic alkali per litre water, drying and treating for ½–2 minutes with 170–220° hot inert gases or steams or with 170–220° hot contact heaters and then rinsing, soaping and drying.

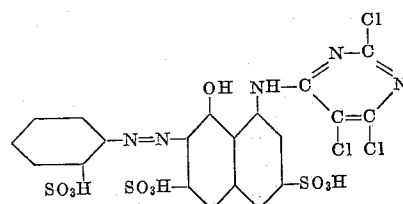
A further modification of the process consists in pre-treating the material, particularly regenerated cellulose fibres, with a solution which contains 50 to 200 g. of an easily water soluble carbamide per litre water, drying, printing with a printing paste which contains per kilogram of paste 2 to 80 g. of reactive dyestuff, 0 to 0.3 mole of basically reacting salts and 0.01 to 0.3 mole of caustic alkali, without or preferably, with 50 to maximally 95 g. easily water soluble carbamide then treating with 170–220° hot inert gases or steams or with 170 to 220° hot contact heaters for ½ to 2 minutes and then rinsing, soaping and drying.

The shortening of the fixing time attained when dyeing and printing cellulose fibres with the use of caustic alkalies and heat treatment at high temperatures is of great importance for the use of reactive dyestuffs as continuous processing is facilitated and productivity can be increased. Disadvantageous side effects, for example the adverse influencing of the fastness to the dyeings or prints or of the tensile strength of the material, do not occur. Often, even deeper and more brilliant dyeings or prints are obtained than by the known processes.

Further details can be seen from the following examples which serve to illustrate the invention. Where not otherwise stated, parts are given as parts by weight. The relationship of parts by weight to parts by volume is as that of grammes to cubic centimetres. The temperatures are in degrees centigrade.

EXAMPLE 1

Cotton is foularded with a solution which, in 1000 parts of water, contains 30 parts of the dyestuff of the formula



90 parts of urea, 20 parts of sodium carbonate and 5 parts of sodium hydroxide solution 36° Bè. The impregnated goods are dried at 80° to a moisture of 15% and fixed for 30 seconds over a contact heater at 220°. To remove non-fixed dyestuff the dyed textile material is rinsed, first cold and then hot, then soaped at the boil for 30 minutes with a solution of 2 parts of curd soap in 1000 parts of water, rinsed and dried. A strong, wet fast, brilliant red dyeing is obtained.

If the process is performed under otherwise the same conditions but without sodium hydroxide, then considerably weaker dyeings are obtained.

On the other hand, an equally good result is obtained if, instead of the 5 parts of sodium hydroxide solution, the corresponding amount of potassium hydroxide solution is used.

Deep, pure, wet fast dyeings are also obtained if in the process described above, a dyestuff given in the following Table I is used.

Table I

No.	Dyestuff	Shade on cellulose fibres
1		Blue.

On the other hand, an equally good result is obtained if instead of sodium hydroxide solution the corresponding amount of potassium hydroxide solution is used.

Deep and pure prints are also obtained if, with otherwise the same procedure as in the above example, one of the dyestuffs given in the following Table III is used.

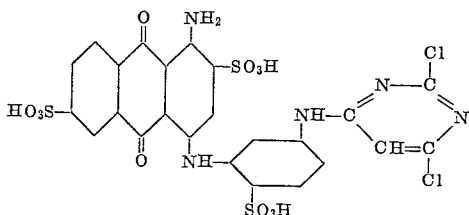
90 parts of urea
210 parts of water
648 parts (5% aqueous solution) of sodium alginate
20 parts of sodium carbonate
2 parts of sodium hydroxide solution 36° Bé.
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1000 parts of printing colour

Table III

No.	Dyestuff	Shade on cellulose fibres
1.		Brilliant red.
2.		Scarlet.
3.		Blue.
4.		Ruby.
5.		Orange brown.

EXAMPLE 4

Staple fibre is impregnated with an aqueous solution which contains per 1000 parts, 100 parts of urea, wrung out to a 100% increase in weight and dried at 80-100°. The fabric previously treated is then printed by one of the usual methods with the following printing colour:
30 parts of the dyestuff of the formula



The textile goods are then dried at 65° to 10% moisture content and afterwards fixed for half a minute in a lyonnair dryer at 210° with hot air. The goods so treated are rinsed, first cold and then hot and then soaped for 30 minutes with a solution of 2 parts of curd soap in 1000 parts of water and again rinsed. A deep, level, brilliant, wet-fast blue print is obtained.

A considerably weaker print is obtained under otherwise the same conditions but without sodium hydroxide in the printing colour.

An equally good result is obtained on the other hand if, instead of sodium carbonate, potassium carbonate is used or if, instead of sodium hydroxide, potassium hydroxide is used.

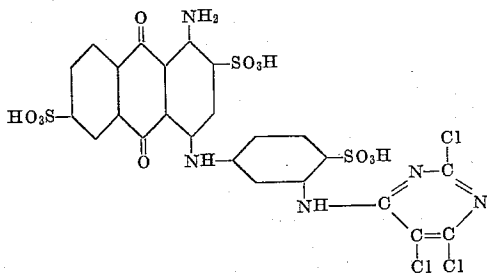
If, under otherwise the same conditions, one of the dyestuffs given in the following Table IV is used, then equally deep level prints are obtained.

Table IV

No.	Dyestuff	Shade on cellulose fibres
1.		Yellow.
2.		Reddish blue.
3.		Greenish black.
4.		Brilliant red.

EXAMPLE 5

Mercerised cotton is soaked in a solution containing 1000 parts of water, 40 parts of the dyestuff of the formula



90 parts of urea and 20 parts of sodium carbonate. Thereupon, the impregnated fabric is dried and resoaked in a solution containing 300 parts of sodium chloride and 10 parts of sodium hydroxide. After pre-drying to a moisture content of 15%, the dyestuff is fixed in a contact heater at 200° for 30 seconds. Finally, the non-fixed dyestuff is removed by rinsing, soaping at the boil for 30 minutes and then rising again. After drying, brilliant blue wet-fast dyeings are obtained.

A similar good result is obtained if sodium carbonate is replaced by potassium carbonate and sodium hydroxide by potassium hydroxide. A considerably weaker dyeing is obtained when the dyestuff is fixed without re-soaking in sodium or potassium hydroxide solution.

What is claimed is:

In a process for fixing reactive dyestuff in cellulose material, comprising impregnating the cellulose material with a liquor containing a reactive dyestuff the reactive grouping of which is the trichloropyrimidyl-(4)-amino radical and urea, pre-drying and then heating the impregnated material and finally rinsing, soaping and drying the same,

the improvement consisting of, in combination,

(a) adding to said impregnating bath per liter thereof from 0.01 to 0.15 mol of caustic alkali, and from 0 to 0.15 mol of a basically reacting salt selected from the group consisting of an alkali metal carbonate, an alkali metal metasilicate, disodium phosphate, trisodium phosphate and tetrasodium pyrophosphate.

(b) pre-drying the impregnated material to a moisture content of about 5% to 25% at about 80° C.,

(c) and thereafter carrying out said heating of the predried material at a temperature of about 220° C. for about 30 seconds.

References Cited in the file of this patent

UNITED STATES PATENTS

3,043,650 Wegmann et al. ----- July 10, 1962

FOREIGN PATENTS

831,371 Great Britain ----- Mar. 30, 1960

OTHER REFERENCES

Caswell: Amer. Dyestuff Reporter, May 18, 1959, pp. 39, 40 and 50.