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PROCESS FOR DYEING AND PRINTING WITH REACTIVE DYESTUFFS

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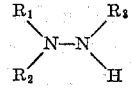
14 Claims. (Cl. 8—54)

The present invention provides a process for dyeing or printing fibrous materials with the aid of reactive dyestuffs or reactive dyestuff intermediates. As is known the term "reactive dyestuffs" describes dyestuffs that enter a covalent bond with the material to be dyed in the course of the dyeing or printing process, and as a rule this is accompanied by elimination of the reactive substituent of the dyestuff. The speed at which the bond between the dyestuff and the substratum is formed depends, on one hand, on the dyeing conditions—such as temperature, pH value of the dyebath or the printing paste—and, on the other, on the reactivity of the reactive grouping of the dyestuff. It is known that in this respect considerable differences exist between individual reactive dyestuffs. The present invention provides a process for increasing the reactivity of reactive dyestuff compounds viz. reactive dyestuffs proper or reactive dyestuff intermediates, wherein there is used a hydrazine containing at least one tertiary nitrogen atom or a water-soluble salt thereof.

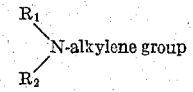
Being a tertiary nitrogen atom, one of the two nitrogen atoms of such a hydrazine grouping must be bound to two carbon atoms, while the other nitrogen atom may be substituted or unsubstituted. There are also suitable cyclic hydrazine compounds, more especially those in which one of the two hydrazine nitrogen atoms, or both, is or are members of one or several rings.

In general, it is of advantage to use a hydrazine or hydrazine salt that is soluble in the dyebath or in the printing paste, and it may contain, in addition to one or more than one hydrazine group, substituents that do not react with the reactive dyestuffs, for example halogen atoms, nitro, alkoxy or hydroxyl groups, but preference is given to such hydrazines as contain, in addition to at least one >N—N< group, only carbon and hydrogen atoms, for example a hydrazine that is substituted exclusively by non-aromatic hydrocarbon radicals and contains at least one tertiary nitrogen atom.

Such hydrazines may correspond, for example, to the formula

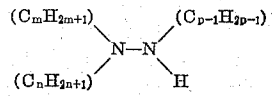
(1) 

in which R_1 and R_2 each represents an aliphatic hydrocarbon radical with at most 4 carbon atoms, and R_3 likewise represents such a radical, an HS–CS group, an HO_3S group, an



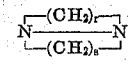
or preferably a hydrogen atom, and R_1 and R_2 together with one nitrogen atom may also form a—preferably, 5-membered to 6-membered—ring.

The purely aliphatic hydrazines of the Formula 1 correspond with advantage to the formula

(2) 

in which m and n each is a whole number not greater than 4, preferably 1, and p is a whole number not greater than 5. The aliphatic hydrocarbon radicals in these hydrazine compounds may be branched, but they are preferably unbranched.

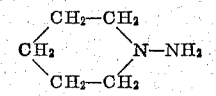
Finally, there may be mentioned especially also those hydrazine compounds whose vicinal nitrogen atoms are at the same time members of two condensed rings, for example those of the formula

(3) 

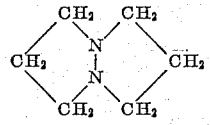
in which r and s may be identical or different and represent the whole numbers 3 or 4.

As specific examples the following hydrazines may be mentioned:

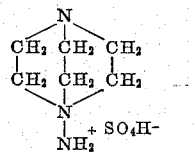
N:N-dimethylhydrazine
N:N:N'-triethylhydrazine
N-aminopiperidine of the formula

(4) 

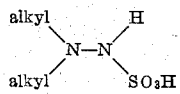
1:5-diaza-bicyclo-(0:3:3)-octane of the formula

(5) 

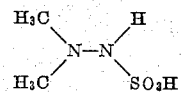
or

(6) 

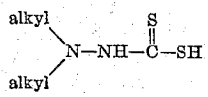
or

(7) 

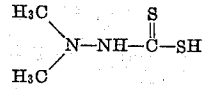
or more especially

(8) 

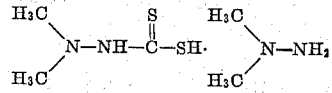
or

(9) 

such as

(10) 

or the hydrazine salt

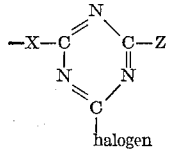
(11) 

If desired, a combination of two or more hydrazines may be used.

The water-soluble salts of the hydrazines—which, if desired may be used for the reaction instead of the free bases—may be derived, for example, from the conventional inorganic or organic acids, for example from sulfuric, hydrochloric, phosphoric, acetic, formic, propionic, chloracetic, oxalic or tartaric acid.

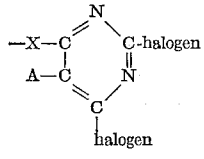
As reactive dyestuffs there are advantageously used in the present process those of the water-soluble variety, for example organic dyestuffs from diazo or coupling components containing carboxyl groups, sulfonic acid groups or aliphatically bound sulfuric acid ester groups. As relevant reactive groupings there may be mentioned the epoxide groups, ethylene imino groups, isocyanate groups, isothiocyanate groups, carbamic acid aryl ester groups, the propiolic acid amide grouping, mono- and dichlorotcrotonylamino, chloroacrylamino, acrylamino, vinylsulfone groups and primarily groupings containing a labile substituent and which are easy to split with entrainment of the bond election pair, for example sulfohalide groups, aliphatically bound sulfuric acid ester groups and aliphatically bound sulfonyloxy groups and halogen atoms, more especially an aliphatically bound chlorine atom. These labile substituents are advantageously in position γ or β of an aliphatic radical which is bound to the dyestuff molecule directly or through an amino, sulfone or sulfonamide group; in those relevant dyestuffs in which the labile substituents are halogen atoms, those mobile halogen atoms may also be present in an aliphatic acyl radical, for example in an acetyl radical, or in position β or in positions α and β of a propionyl radical or preferably in a heterocyclic radical, for example in a pyrimidine or pyridazine ring, or above all in a triazine ring. The dyestuffs contain with advantage a grouping of the formula

(12)



or

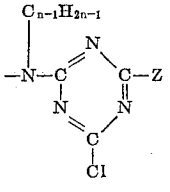
(13)



in which X represents a nitrogen bridge and Z a hydrogen atom, a possibly substituted amino group, an etherified hydroxyl or mercapto group or a halogen atom or an alkyl, aryl or aralkyl group, and A stands for a hydrogen atom or a halogen atom. The halogen atoms are, for example, bromine atoms or preferably chlorine atoms.

It is of special value to use dyestuffs that contain the grouping of the formula

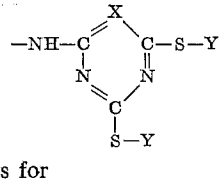
(14)



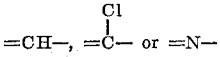
in which n is a whole number not greater than 4 and Z has the above meaning.

Further suitable are dyestuffs containing diphenoxytriazine groupings and those which contain a grouping of the formula

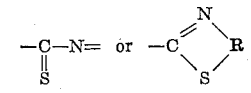
(15)



in which X stands for



and Y stands for a group



in which R represents an ortho-arylene radical.

Further suitable reactive groupings are the following radicals: Trichloropyridazine, dichloroquinoxaline, dichlorobutene, halogenated pyridazone, sulfonic acid dichloropropylamide, allylsulfone, allylsulfide, 2-halogenbenzthiazolecarbamide, isothiocyanate and β-sulfatopropionic acid amide radicals.

The present process may be performed with a wide variety of organic dyestuffs, for example oxazine, triphenylmethane, xanthene, nitro, accridone, azo, anthraquinone and phthalocyanine dyestuffs.

From the azo dyestuff series there may be mentioned, for example, disazo and trisazo dyestuffs, and more especially monoazo dyestuffs. A large number of such active azo dyestuffs is already known so that there is no need to deal with them in greater detail here.

From the series of the anthraquinone dyestuffs there may be mentioned primarily the 1-amino-4-bromanthraquinone-2-sulfonic acid and the dyestuffs derived from 1:4 - diaminoanthraquinone - 2 - sulfonic acid. These and other anthraquinone dyestuffs are manufactured in known manner. As suitable phthalocyanine dyestuffs there may be mentioned above all dyestuffs which are derived from nickel or copper phthalocyanine sulfonamides and contain at least two free sulfonic acid groups per molecule and which contain at least in one sulfonamide radical a group with at least one labile halogen atom.

The present process may also be performed with vat dyestuffs that are water-soluble or insoluble in the oxidized form and dispersion dyestuffs having the characteristics of reactive dyestuffs.

There are several favorable variants available for the performance of the present process. Inter alia, there may be used different proportions, for example for every reactive group of one molecular proportion of a dyestuff at least 1 molecular proportion of the hydrazine compound, or for the same amount of dyestuff less than 1 molecular proportion of hydrazine compound may be used. It is also possible to quaternate the dyestuff with the hydrazine compound, in which case the ratio quaternated dyestuff: dyebath is so that the amount of hydrazine compound present in the quaternated dyestuff corresponds to that amount of hydrazine compound which would have to be added in the unquaternated state to the dyebath or to the printing paste. In connection with both ratios—and more especially in the case of the ratio named first (which is hereinafter referred to as the stoichiometric ratio)—there may be distinguished three methods, namely:

(a) For dyeing or printing the fibrous material use is made of reaction products of reactive dyestuffs and a hydrazine containing at least one tertiary nitrogen atom;

(b) The fibrous material is dyed or printed with a preparation manufactured from a reactive dyestuff and a hydrazine containing at least one tertiary nitrogen atom;

(c) The reactive dyestuff and the hydrazine containing at least one tertiary nitrogen atom are applied separately to the fibrous material.

For the method described under (a) it is necessary to prepare reaction products of reactive dyestuffs with hydrazines containing at least one tertiary nitrogen atom; they are accessible, for example, by treating the substituted hydrazine with the reactive dyestuff in an aqueous medium at room temperature or at a slightly higher temperature. If desired, these products may be isolated, for example salted out.

Variant (b) is suitable not only for a stoichiometric ratio but also particularly for a ratio in which for every

reactive group of a mol of dyestuff less than one mol of hydrazine compound is used; it is especially suitable for a catalytic ratio. As is usual "catalytic ratio" describes a ratio which is substantially smaller than the ratio referred to under (a). The amount of hydrazine compound referred to the reactive dyestuff may, however, vary within certain limits and depends on the reactivity of the hydrazine used. Referred to the amount of dyestuff the catalytic amount of hydrazine compound may vary from about 0.1 to 10% and preferably from about 0.2 to 2% by weight.

In variant (c), in which the hydrazine compound may be used in a stoichiometric or a catalytic ratio, the reactive dyestuff and the hydrazine are applied in any desired order of succession to the fibrous material, if desired with the use of intermediate drying.

In other respects it is immaterial whether and to what extent the reaction of the reactive dyestuff with the hydrazine compound by any one of the different variants and in the different ratios gives rise to other reactions, such as formation of quaternary ammonium compounds.

What has been said above with regard to the reactive dyestuffs applies in appropriate manner also to the reactive intermediates, for example reactive coupling components.

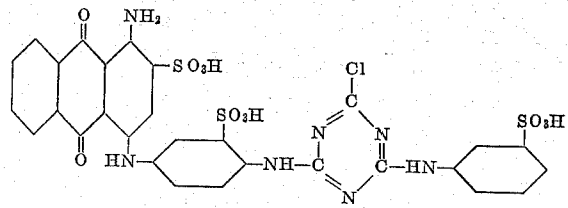
The present process is suitable for dyeing or printing a wide variety of fibrous materials such as paper or leather or above all textile materials, for example those made from animal fibers such as silk, and above all those from cellulose fibers, including both native cellulose fibers such as linen or cotton and fibers from regenerated cellulose such as rayon (viscose) or rayon staple. In other respects dyeing and printing are carried out under the conditions conventionally used for reactive dyestuffs, more especially also when a catalytic proportion of the hydrazine compound is used. For dyeing and printing cellulosic textile materials it is of special advantage to use concomitantly inorganic acid acceptors, such as carbonates, hydroxides, bicarbonates or phosphates of alkali metals, or mixtures thereof. Also bases such as trimethyl benzyl ammonium hydroxide or sodium trichloracetate. When reactive vat dyestuffs are used, the process may be performed in the presence of a conventional reducing agent such as sodium hydrosulfite, thiourea dioxide, sodium sulfide or sodium sulfoxylate. It is also possible to incorporate with the dyebaths and printing pastes the conventional additives, such as electrolytes, for example sodium chloride, sodium acetate, or non-electrolytes such as urea or thickeners, such as alginates. To prevent undesirable reduction phenomena, more especially in the dyestuffs, use may be made of one of the conventional additives, such as meta-nitrobenzenesulfonic acid. As a rule the hydrazine is added to the dyebath or to the printing paste. If dyeing is carried out as a two-stage process—the application of the dyestuff and the fixation with the acid acceptor being performed separately—it is possible to add the hydrazine only in the second stage of the process. When dyeing or printing is carried out in a neutral to acidic medium, for example in the case of nitrogenous textile fibers or leather, it is of advantage to use a water-soluble hydrazine salt, and the same applies to the case where at the same time a finishing operation with a curable aminoplast, for example a condensation product of formaldehyde with melamine or urea, is carried out.

As mentioned above, the fibrous materials are dyed or printed under the conditions conventionally used for reactive dyestuffs. The present process allows the reaction times and/or the reaction temperature to be reduced and/or dyeings and prints of greater tinctorial strength to be produced, for example by the cold pad batch method, by the pad-steam or pad-dry method, by the wet-pad steam process and more especially by the exhaustion method and in printing. Depending on the method used, the dyestuffs may be fixed at widely differing temperatures, for example from 20 to 200° C. or higher, for example at a temperature ranging from 250 to 300° C.

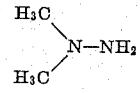
Unless otherwise indicated, parts and percentages in the following examples are by weight. As a rule, the dyestuffs are shown as the free acids, but they are actually used in the form of the alkali metal salts.

Example 1

A solution of 30 parts of the dyestuff of the formula



in 800 parts of boiling water is cooled to 20° C. and mixed with 10 parts by volume of a sodium hydroxide solution of 30% strength, 20 parts of crystalline sodium sulfate and 0.05 to 0.2 part of N:N-dimethyl hydrazine of the formula



whereupon the resulting solution is made up with cold water to 1000 parts.

A cotton fabric is padded with the above solution to a weight increase of 75%, immediately reeled up and left to itself in this state for 6 to 12 hours at 20° C., after which the unfixed portion of the dyestuff is removed by a thorough rinse in cold and in boiling water and finally soaped in the usual manner.

The resulting blue dyeing displays good fastness to light and washing and is substantially more intense than a comparable dyeing produced without addition of N:N-dimethylhydrazine.

When 15 parts of trisodium phosphate are used instead of 10 parts by volume of sodium hydroxide solution, good results are likewise obtained.

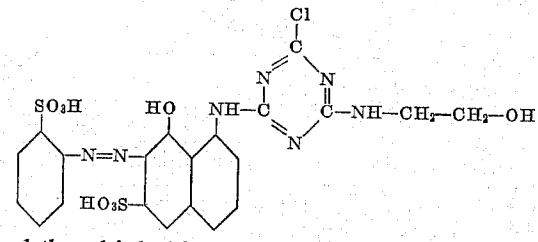
With equal results there may be used 2 parts of dimethylhydrazine instead of 0.05 to 0.2 part thereof.

Similar good results are obtained by using 1:5-diazabicyclo-(0:3:3)-octane instead of N:N-dimethylhydrazine.

By using for every 1000 parts of dyebath 4 parts of a solution containing in 99 parts of a 5% aqueous dimethylhydrazine solution, 1 part of sodium sulfite, and 20 parts of sodium carbonate instead of 0.05 to 0.2 part of dimethylhydrazine and 10 parts by volume of 30% sodium hydroxide solution, similar good results are obtained.

Example 2

A cotton fabric is impregnated at 50° C. with a padding solution which contains per 1000 parts of water 25 parts of the dyestuff of the formula

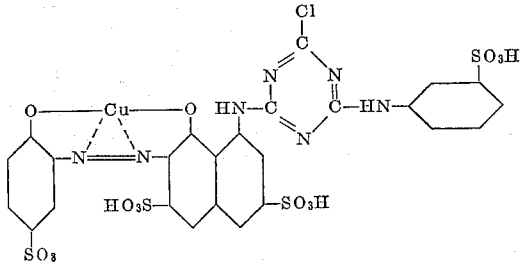


and then dried. After drying, the fabric is padded with a solution containing for every 1000 parts of water 200 parts of calcined sodium sulfate, 10 parts by volume of sodium hydroxide solution of 30% strength and 0.05 to 0.2 part of N:N-dimethylhydrazine. The reeled up material is kept for 3 to 6 hours at room temperature and then finished off as described in Example 1.

The resulting brilliant red dyeing is distinctly of greater tinctorial strength than a comparable dyeing produced without N:N-dimethylhydrazine. The results achieved are equally good when instead of 0.05 to 0.2 part 2 parts of dimethylhydrazine are used. It is also possible to quaternate 3 of the 25 parts of dyestuff used with 0.2 part of N:N-dimethylhydrazine and to add this product together with the remaining 22 parts of unquaternated dyestuff to the padding solution. When the 0.05 to 0.2 part of N:N-dimethylhydrazine is then omitted from the dyebath, all remaining conditions being identical, a similar, good dyeing is obtained.

Example 3

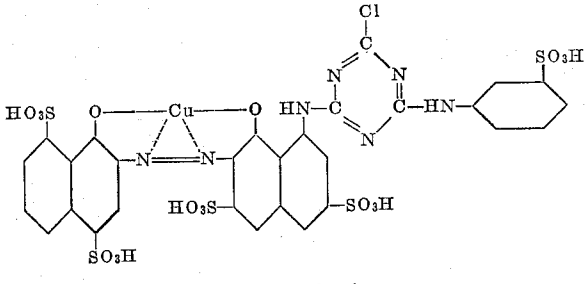
A solution of 1.5 parts of the dyestuff of the formula



in 250 parts of boiling water is added to a dyebath containing in 750 parts of water 60 parts of sodium chloride. The resulting dyebath is used to dye 50 parts of cotton yarn for 30 minutes at 40° C. The fixation of the dyestuff deposited on the fiber is carried out following upon this exhaustion process in the same dyebath after addition of 15 parts of trisodium phosphate and 0.02 part of N:N-dimethylhydrazine. Fixing takes 1½ hours at 40° C. The dyed yarn is thoroughly rinsed in cold and in hot water and finally soaped at the boil.

A brilliant violet dyeing is obtained which possesses good fastness properties and is of considerably greater tinctorial strength than a comparable dyeing produced in the absence of N:N-dimethylhydrazine.

When the dyestuff used above is replaced by an equivalent amount of the dyestuff of the formula



good results are likewise obtained.

Similar, good results are obtained by using N:N:N'-trimethylhydrazine instead of N:N-dimethylhydrazine.

Example 4

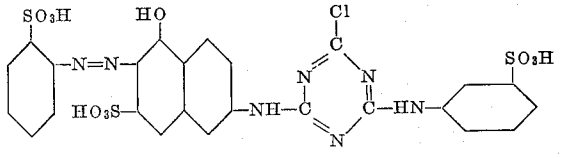
A mixture of 30 parts of the dyestuff mentioned in Example 2 and 50 parts of urea is dissolved in 700 parts of boiling water. This solution is cooled to 40° C., 20 parts of sodium carbonate and 0.2 part of N:N-dimethylhydrazine are added, and the solution is made up with cold water to 1000 parts.

A cotton fabric is padded with the above solution to a weight increase of 75% and then steamed directly, that is to say without being intermediately dried, for 1 minute. The steamed fabric is rinsed and soaped in the usual manner.

The resulting brilliant red dyeing has very good fastness to light and washing. The same procedure, except that N:N-dimethylhydrazine is omitted, gives a considerably weaker dyeing.

Example 5

A mixture of 20 parts of the dyestuff of the formula



and 40 parts of urea is dissolved in 600 parts of boiling water. The solution is cooled to 40° C., 20 parts of sodium carbonate and 0.2 part of N:N-dimethylhydrazine are added, and the whole is made up with cold water to 1000 parts.

A cotton fabric is padded with this solution to a weight increase of 70%. The fabric is then reeled up and kept for 1 hour in a pad-roll installation at a temperature of 80° C. measured with a wet-bulb thermometer then thoroughly rinsed in cold and in hot water and soaped at the boil.

The resulting deep orange dyeing has very good fastness to light and washing and greater tinctorial strength than a comparable dyeing produced without addition of N:N-dimethylhydrazine.

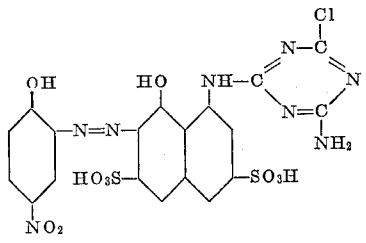
Example 6

A solution of 3 parts of the dyestuff of Example 1 in 100 parts of water is used to impregnate a cotton fabric to a weight increase of 70%. After an intermediate drying the fabric is impregnated with a solution of 250 parts of sodium chloride, 6 parts of sodium hydroxide 100% and 1 part of N:N-dimethylhydrazine in 900 parts of water, to achieve a weight increase of 80%. Immediately thereafter the fabric is steamed for 30 seconds with steam heated at 103 to 110° C., then thoroughly rinsed in cold and in hot water, washed for 5 minutes at the boil with addition of soap and then dried.

The resulting brilliant blue dyeing has very good fastness to light and washing. A comparably produced dyeing without addition of N:N-dimethylhydrazine is substantially weaker.

Example 7

A mixture of 40 parts of the 1:2-chromium complex of the dyestuff of the formula



and 200 parts of urea is dissolved in 870 parts of hot water and the solution is cooled to room temperature, and 20 parts of sodium carbonate and 1 part of N:N-dimethylhydrazine are then stirred into the solution. This solution is used to impregnate a mercerized cotton fabric to a weight increase of 70%. The fabric is then dried in a current of hot air to a residual moisture content of 8%, then thoroughly rinsed in cold and in boiling water, and dried.

The resulting covered greenish blue dyeing has very good wet fastness properties.

The same method, but without addition of N:N-dimethylhydrazine, yields a substantially lighter tint.

Example 8

A printing paste is prepared from the following ingredients:

	Parts
Dyestuff of Example 2	50
Urea	200
Water	379.5
Sodium alginate thickening 50:1000	350
Sodium bicarbonate	10
N:N-dimethylhydrazine	0.5
Sodium meta-nitrobenzenesulfonate	10
	1000

A cotton fabric is printed with this printing paste on a roller printing machine, then dried and steamed for 3 minutes at 100° C. in a Mather-Platt ager. The fixed print is rinsed in cold and in hot water and dried. The resulting print is of equal tinctorial strength to that obtained by fixing for 8 minutes without addition of N:N-dimethylhydrazine.

A similar result is obtained on a spun rayon fabric.

Example 9

A printing paste is prepared from the following ingredients:

	Parts
Dyestuff mentioned in Example 1	50
Urea	200
Water	378
Sodium alginate thickening 50:1000	350
Sodium bicarbonate	10
N:N-dimethylhydrazine	2
Sodium meta-nitrobenzenesulfonate	10
	1000

The above printing paste is applied by means of a roller printing machine to a cotton fabric. The fabric is dried and then fixed for 30 seconds in a rapid ager, and then finished off as described in Example 8.

The resulting blue print is of equal tinctorial strength to that obtained by fixing for 8 minutes in the absence of N:N-dimethylhydrazine. A similar result is obtained on a spun rayon fabric.

Example 10

A printing paste is prepared from the following ingredients:

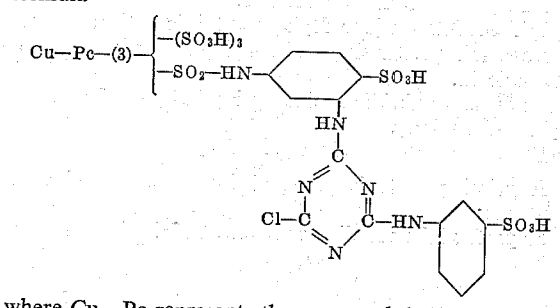
	Parts
Dyestuff of the formula shown below	50
Urea	200
Water	328
Sodium alginate thickening 50:1000	350
Aqueous potassium carbonate solution of 50% strength	60
N:N-dimethylhydrazine	2
Sodium meta-nitrobenzenesulfonate	10
	1000

A cotton fabric is printed with the above printing paste on a roller printing machine, dried and then steamed for 30 seconds in a rapid ager. The fabric is then finished off as described in Example 8.

The resulting turquoise print has substantially greater

tinctorial strength than when fixed for 8 minutes without addition of N:N-dimethylhydrazine.

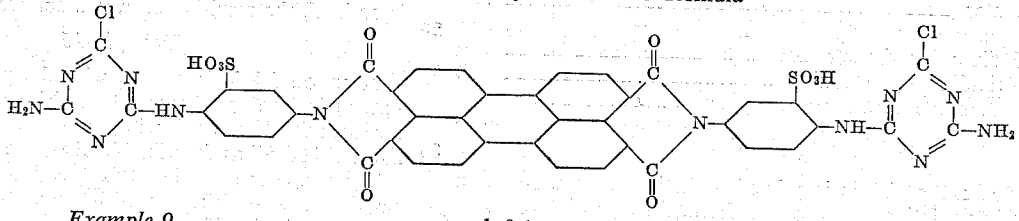
The dyestuff used in this example corresponds to the formula



where Cu—Pc represents the copper phthalocyanine residue.

Example 11

A cellulose fabric is padded at 20 to 30° C. with a solution containing per 1000 parts of water 10 parts of sodium hydroxide solution of 30% strength, 20 parts of the dyestuff of the formula



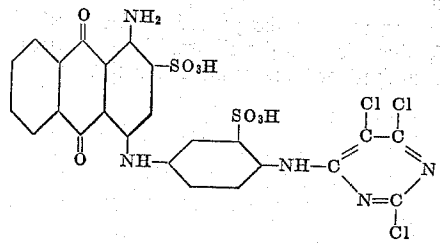
and 0.1 part of N:N-dimethylhydrazine. The fabric is then reeled up, wrapped in a plastic film, stored for 6 hours, then rinsed, oxidized, soaped at the boil, once more rinsed and dried. The resulting red dyeing is fast to washing at the boil. Similar results are obtained by using 10 parts of sodium sulfide instead of 10 parts of sodium hydroxide solution of 30% strength.

Example 12

A mercerized cotton fabric is padded to a weight increase of 70% with a solution containing per 1000 parts of water 30 parts of the dyestuff mentioned in Example 1. With or without being subjected to intermediate drying the impregnated fabric is then fixed for 2 minutes at 80° C. in a bath containing in 1000 parts of water 15 parts of trisodium phosphate, 200 parts of sodium chloride and 0.5 part of N:N-dimethylhydrazine. The fixed fabric is thoroughly rinsed in cold and in boiling water and soaped as usual. The resulting deep blue dyeing has good properties of fastness.

A comparable dyeing produced without addition of N:N-dimethylhydrazine displayed a much weaker tint.

When the dyestuff used above is replaced by the dyestuff of the formula



(prepared by condensing the basic anthraquinone dyestuff with tetrachloropyrimidine in an aqueous medium at a pH value from 6 to 9) similar, good results are obtained.

Example 13

A cotton fabric is padded at room temperature to a weight increase of 70% with a solution containing per 1000 parts of water 0.5 part of N:N-dimethylhydrazine.

The fabric so pretreated is then impregnated with a dyestuff solution containing per 1000 parts of water 30 parts of the dyestuff used in Example 1, 50 parts of urea and 20 parts of sodium carbonate.

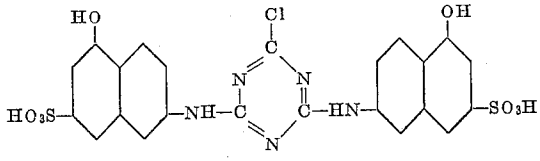
Without intermediate drying the fabric is then steamed for one minute. Rinsing and soaping is performed as in Example 12.

The resulting brilliant blue dyeing has good fastness to light and washing.

Example 14

A printing paste is prepared from the following ingredients:

50 parts of the coupling component of the formula



	Parts
Urea	200
Water	358
Sodium alginate thickening 50:1000	370
Sodium bicarbonate	10
N:N-dimethylhydrazine	2
Sodium meta-nitrobenzenesulfonate	10
	1000

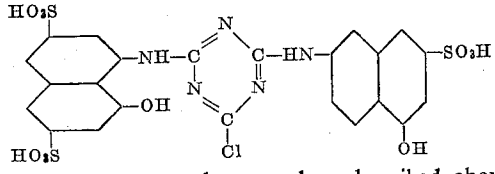
A cotton fabric is printed with the above paste on a roller printing machine and dried, then fixed for 30 seconds in a rapid ager, and rinsed in cold and in hot water. The resulting colorless prints obtained in this manner are developed for 10 minutes at 25° C. in a bath containing per 1000 parts of water 2 parts of diazotized ortho-chloraniline, then thoroughly rinsed in cold and in hot water.

The resulting orange print has good properties of general fastness. When N:N-dimethylhydrazine is omitted, a weaker print results.

When ortho-chloraniline is replaced by 2 parts of diazotized ortho-nitraniline, an orange print is obtained which has identical properties.

When ortho-chloraniline is replaced by 2 parts of para-nitro-ortho-anisidine, a red print is obtained which has identical properties.

When the printing paste is prepared with the coupling component of the formula



and in other respects the procedure described above is adopted, diazotized ortho-chloraniline produces a red print, diazotized ortho-nitraniline a bluish red print and

diazotized para-nitro-ortho-anisidine a violet print in good yield.

When N:N-dimethylhydrazine is omitted, the resulting prints are weaker.

Example 15

A printing paste is prepared from the following ingredients:

	Parts
Dyestuff used in Example 2	50
Urea	200
Water	378
Sodium alginate thickening 50:1000	350
Sodium bicarbonate	10
N:N-dimethylhydrazine	2
Sodium meta-nitrobenzenesulfonate	10
	1000

A cotton fabric is printed with this paste with the aid of a roller printing machine and then, without intermediate drying, fixed for 2 minutes in dry heat at 150° C. The fabric is finished off as described in Example 1.

A red print is obtained. When N:N-dimethylhydrazine is omitted, the resulting print is much weaker.

Example 16

A cotton fabric is printed with the printing paste described in Example 15 and then dried. The dried prints are fixed for 10 seconds with the aid of an infra-red drier and finished off as described in Example 1.

The resulting red print is as strong as the print of Example 15. When N:N-dimethylhydrazine is omitted, the resulting print is of inferior tinctorial strength.

Example 17

A cotton fabric printed with the printing paste of Example 15, dried and then fixed for one minute in dry heat and finished off as described in Example 1.

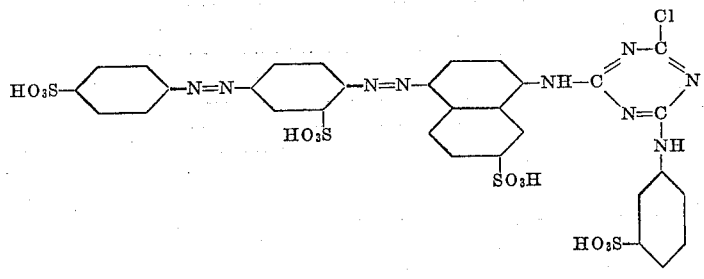
The resulting red print is as strong as that obtained in Example 15. When N:N-dimethylhydrazine is omitted a substantially weaker print results.

Example 18

A solution of 0.6 part of the dyestuff used in Example 2 in 100 parts of hot water is added to a dyebath containing in 900 parts of water 50 parts of sodium chloride. 20 parts of natural silk are dyed in the resulting dyebath for 30 minutes at 40° C. The dyestuff which has only been absorbed by the fiber is fixed by the addition of 2 parts of sodium carbonate and 0.06 part of N:N-dimethylhydrazine for 90 minutes, likewise at 40° C.; the fabric is then thoroughly rinsed in cold and in hot water and finally soaped at 70° C.

The resulting brilliant red dyeing is fast to light and washing and of much greater tinctorial strength than a comparable dyeing produced without addition of N:N-dimethylhydrazine.

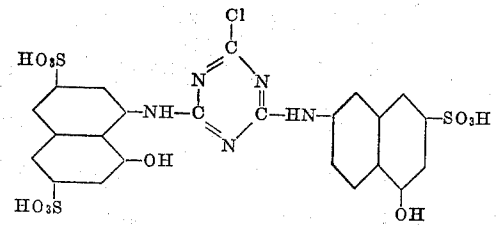
When the dyestuff used above is replaced by an equivalent amount of the disazo-dyestuff of the formula



a yellowish brown dyeing is obtained.

Example 19

A solution of 40 parts of the coupling component of the formula



in 929.8 parts of water is mixed with 10 parts of a sodium hydroxide solution of 30% strength, 20 parts of crystalline sodium sulfate and 0.2 part of N:N-dimethylhydrazine.

A mercerized cotton fabric is padded with the above solution, reeled up and stored for 3 hours at a constant temperature of 30° C. After this storing the unfixed portion of dyestuff is washed out by thoroughly rinsing the fabric in cold and in hot water.

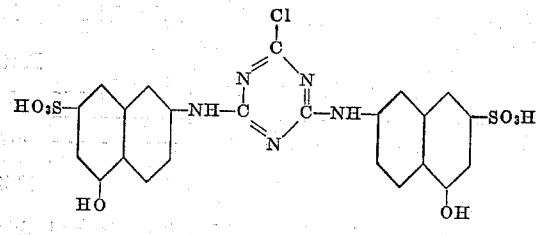
The fabric impregnated in this manner is then developed with a freshly prepared solution containing in 1000 parts of water 2 parts of the diazo compound of meta-chloraniline. After coupling the fabric is rinsed and soaped at the boil. The resulting brilliant scarlet dyeing has good fastness to washing and rubbing.

A comparable dyeing produced without addition of N:N-dimethylhydrazine is considerably weaker.

When the development is carried out with 2 parts (per 1000 parts of water) of diazotized para-nitro-ortho-anisidine instead of with meta-chloraniline, a deep claret dyeing is obtained which has good properties of general fastness and is likewise substantially stronger than a comparable dyeing produced without addition of N:N-dimethylhydrazine.

Example 20

A mixture of 6 parts of the coupling component of the formula



and 60 parts of sodium chloride is dissolved in 1000 parts of water at 70° C. This solution is used to dye 50 parts of cotton tricot for 30 minutes at a temperature of 70° C. The fabric is then fixed in the same bath after addition of 15 parts of crystalline trisodium phosphate and 0.2 part of N:N-dimethylhydrazine for 90 minutes at 70° C. After this exhaustion treatment the unfixed portion of the coupling component is washed out in cold and in hot water.

The tricot treated in this manner is then coupled in a solution containing per 1000 parts of water 2 parts of the freshly prepared diazo compound para-nitro-ortho-anisidine and finished off as described in Example 1.

The resulting strong brilliant red dyeing has good properties of fastness.

A dyeing produced in identical manner but without addition of N:N-dimethylhydrazine was found to be substantially inferior in tinctorial strength.

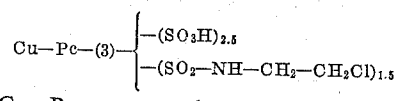
Example 21

A mercerized cotton fabric is padded at 40° C. with a solution containing per 1000 parts of water 30 parts of the dyestuff used in Example 1, 200 parts of urea, 20 parts of sodium carbonate and 0.5 part of N:N-dimethylhydrazine. To fix the dyeing the impregnated fabric is exposed to the action of a high-frequency electric field; it is then rinsed in cold and in hot water, soaped at the boil, once more rinsed and dried.

The resulting fast, deep blue dyeing is of greater tinctorial strength than a comparable dyeing produced without addition of N:N-dimethylhydrazine.

Example 22

A cotton fabric is padded at 40° C. with a solution containing in 1000 parts of water, 30 parts of the dyestuff of the formula



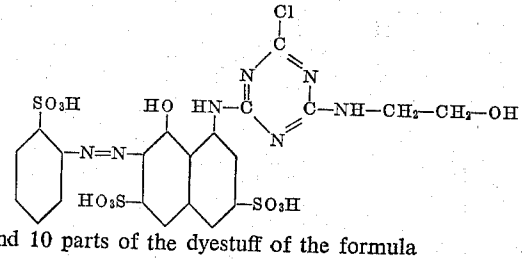
(where Cu—Pc represents the residue of copper phthalocyanine), 50 parts of urea, 20 parts of sodium carbonate and 0.2 part of N:N-dimethylhydrazine. The fabric is then dried at 60 to 80° C. and steamed for 30 seconds, then rinsed in cold and in hot water and soaped at the boil.

The resulting turquoise dyeing has good properties of fastness.

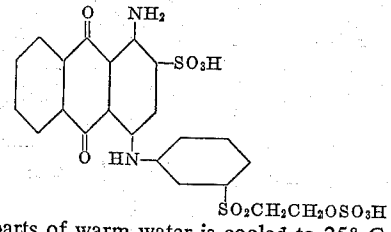
A dyeing produced in identical manner but without addition of N:N-dimethylhydrazine revealed a substantially inferior exhaustion.

Example 23

A solution of 10 parts of the dyestuff of the formula



and 10 parts of the dyestuff of the formula

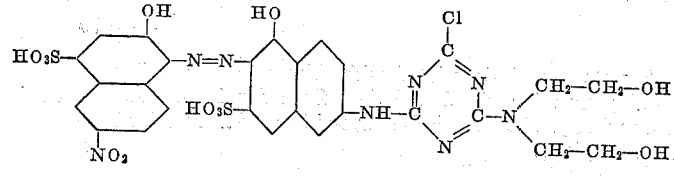


in 800 parts of warm water is cooled to 25° C. and then mixed with 15 parts of trisodium phosphate, 5 parts by volume of a sodium hydroxide solution of 30% strength and 0.2 part of N:N-dimethylhydrazine. The whole is then made up with cold water to 1000 parts by volume.

A cotton fabric is impregnated with the above solution, immediately reeled up and so kept for 4 hours at 25° C. After this storing the unfixed portion of dyestuff is washed out by thoroughly rinsing the fabric in cold and in hot water and the fabric is then soaped at the boil.

The resulting violet dyeing is much deeper than when N:N-dimethylhydrazine is omitted.

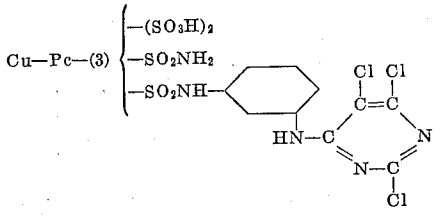
When the above dyestuff mixture is replaced by 20 parts of the 1:2-chromium complex in which 2 molecules of the dyestuff of the formula



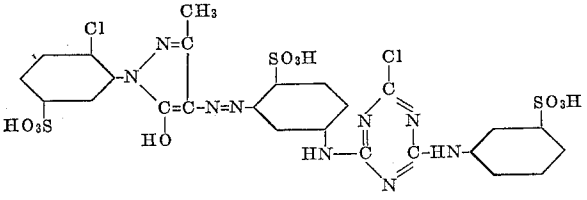
are bound to one atom of chromium, a deep black dyeing is obtained which has good properties of fastness.

Example 24

A mixture of 30 parts of the dyestuff of the formula



(where Cu—Pc represents the copper phthalocyanine residue) and 20 parts of the dyestuff of the formula



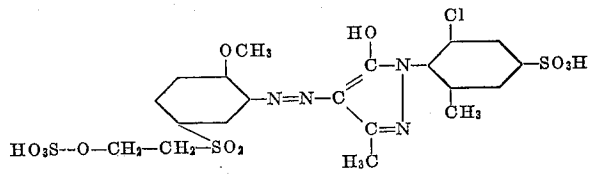
is dissolved in 800 parts of boiling water; the solution is cooled to 25° C. and mixed with 16 parts of trisodium phosphate, 8 parts by volume of sodium hydroxide solution of 30% strength and 0.2 part of N:N-dimethylhydrazine. The whole is then made up with cold water to 1000 parts by volume.

A cotton fabric is padded with this solution to a weight increase of 70%, reeled up and kept for 6 hours at a constant temperature of 25° C. The stored material is thoroughly rinsed in cold and in hot water and finally soaped at the boil.

A brilliant yellowish green dyeing is obtained. A comparable combination dyeing produced without addition of N:N-dimethylhydrazine displays weaker tints.

Example 25

When the dyestuffs shown in Example 24 are replaced by a combination of 30 parts of the dyestuff of Example 10 and 20 parts of the dyestuff of the formula



and dyeing is performed in identical manner, similar good results are obtained.

Example 26

A printing paste is prepared from the following ingredients:

	Parts
Dyestuff of the formula of Example 22	50
Urea	200
Water	328
Sodium alginate thickening 50:1000	350
Aqueous potassium carbonate solution of 50% strength	60
N:N-dimethylhydrazine	2
Sodium meta-nitrobenzenesulfonate	10
	1000

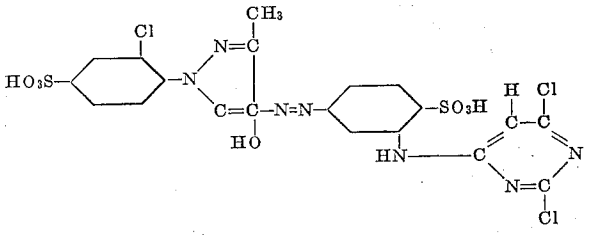
A cotton fabric is printed with this paste on a roller printing machine, dried and then fixed for 30 seconds in a rapid ager. The fabric is then finished off as described in Example 1.

The resulting turquoise print has good properties of fastness and is substantially stronger than when N:N-dimethylhydrazine is omitted.

Example 27

A printing paste is prepared from the following ingredients:

50 parts of the dyestuff of the formula



(obtained by condensing the basic aminoazo dyestuff with 2:4:6-trichloropyrimidine)

	Parts
Urea	100
Water	428
Sodium alginate thickening 50:1000	400
Sodium bicarbonate	10
N:N-dimethylhydrazine	2
Sodium meta-nitrobenzenesulfonate	10
	1000

A cotton fabric is printed with this paste on a roller printing machine or by the screen printing method. The fabric is dried and then fixed for 30 seconds in a rapid ager and finished off as described in Example 1. The resulting yellow print is of much greater tinctorial strength than when N:N-dimethylhydrazine is omitted.

Example 28

A printing paste is prepared from the following ingredients:

	Parts
Dyestuff of the formula shown in Example 22	30
Water	420
Sodium alginate thickening 50:1000	550
	1000

A cotton fabric is printed with this paste and then dried. The dried fabric is padded with a solution containing in 1000 parts of water 150 parts of sodium chloride, 100 parts of potassium carbonate, 30 parts by volume of a sodium hydroxide solution of 30% strength and 2 parts of N:N-dimethylhydrazine and squeezed to a residual liquor content of 70%, then without intermediate drying fixed for 30 seconds in a rapid ager and finished off as described in Example 1.

The resulting turquoise print is of considerably greater tinctorial strength than when N:N-dimethylhydrazine is omitted.

A similar, good result is obtained on a spun rayon fabric.

Example 29

A printing paste is prepared from the following ingredients:

	Parts
Dyestuff of the formula shown in Example 22	30
N:N-dimethylhydrazine	2
Water	418
Sodium alginate thickening 50:1000	550
	1000

A spun rayon fabric is printed with this paste, then dried and padded with a solution containing in 1000 parts of water 150 parts of sodium chloride, 100 parts of potassium carbonate and 30 parts by volume of a sodium hydroxide solution of 30% strength, squeezed on a padder to a residual liquor content of 70% and then, without intermediate drying, fixed in a rapid ager for 30 seconds. The fabric is then finished off as described in Example 1.

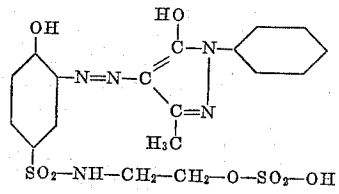
The resulting turquoise print is of good tinctorial strength. When the same procedure is followed but without addition of N:N-dimethylhydrazine, a considerably weaker print results.

An equally good result is obtained on a cotton fabric.

Example 30

A printing paste is prepared from the following ingredients:

20 parts of the 1:2-cobalt complex of the dyestuff of the formula



	Parts
Urea	100
Water	468
Sodium alginate thickening 50:1000	350
Sodium bicarbonate	50
N:N-dimethylhydrazine	2
Sodium meta-nitrobenzenesulfonate	10
	1000

A cotton fabric is printed with this paste on a roller printing machine and dried, then fixed for 30 seconds in a rapid ager and finished off as described in Example 1.

The resulting yellowish brown print is of considerably greater tinctorial strength than when N:N-dimethylhydrazine is omitted and has good properties of fastness.

Example 31

A solution of 4 parts of the dyestuff used in Example 1 in 100 parts of water is used to pad a cotton fabric to a weight increase of 70%.

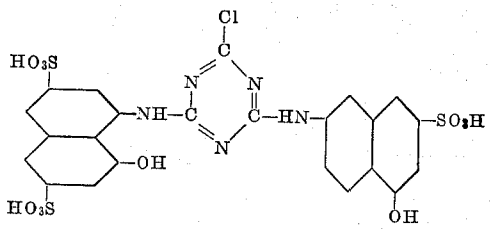
After an intermediate drying the fabric is conveyed through a solution of 250 parts of sodium chloride, 6 parts of sodium hydroxide of 100% strength and 1 part of N:N-dimethylhydrazine in 900 parts of water. This bath is located over one leg of a molten metal bath shaped in the form of a U. The chemical solution and the metal bath have a temperature of 90° C. The fabric is first conveyed through the chemical bath and immediately thereafter through the metal bath. The time of residence of the fabric in the metal bath is 7 to 10 seconds. After it has left the metal bath the fabric is thoroughly rinsed in cold water and then for about 10 minutes in boiling water, and dried.

The resulting strong, blue dyeing has good properties of fastness.

When the same procedure is adopted but the N:N-dimethylhydrazine is omitted from the chemical bath, a pale lilac dyeing results.

Example 32

A solution of 40 parts of the coupling component of the formula



in 500 parts of water is mixed with a solution of 20 parts of the dyestuff of the formula shown in Example 1 in 449.8 parts of water, 30 parts by volume of a sodium hydroxide solution of 30% strength, 20 parts of crystalline sodium sulfate and 0.2 part of N:N-dimethylhydrazine.

A cotton fabric is padded with this solution, then reeled up and stored for 3 hours at a constant temperature of 30° C. After this storing the unfixed dyestuff is washed out by rinsing the fabric thoroughly in cold and in hot water.

The impregnated fabric is then coupled with a freshly prepared solution containing in 1000 parts of water 2 parts of the diazo compound of meta-chloraniline.

The resulting deep claret dyeing has good fastness to washing and rubbing.

A comparable dyeing produced without addition of N:N-dimethylhydrazine was of much weaker tinctorial strength.

Example 33

100 parts of a cotton fabric are immersed at 25° C. in a bath which contains in 3000 parts of water 1 part of the dyestuff of the formula shown in Example 2. In the course of 30 minutes 150 parts of sodium chloride, then 25 parts of anhydrous sodium carbonate and after another 5 minutes 10 parts of N:N-dimethylhydrazine are added. The fabric remains for 1 hour in the dyebath and is then rinsed and soaped in the usual manner. A red dyeing is obtained.

Without adding N:N-dimethylhydrazine a substantially weaker dyeing results.

Example 34

100 parts of a cotton fabric are padded with a solution which contains in 1000 parts of water 20 parts of the dyestuff of the composition shown in Example 2 and 50 parts of sodium chloride, and then expressed to a weight increase of 100%. The fabric is then immersed for 10 seconds in a solution containing in 1000 parts of water 10 parts of N:N-dimethylhydrazine and 50 parts of sodium chloride, and finally rinsed and soaped in the usual manner. A strong red dyeing is obtained which is much stronger than a comparably produced dyeing in the absence of N:N-dimethylhydrazine.

Example 35

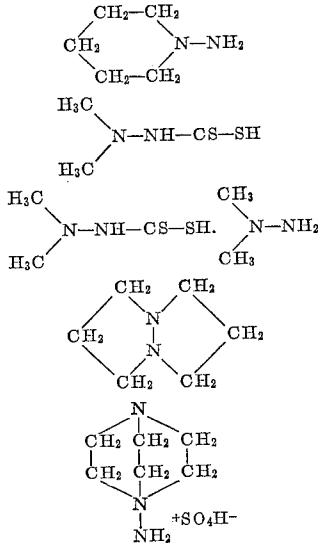
70 parts of the dyestuff of the formula shown in Example 2 are dissolved in 2000 parts of water, mixed with 8 parts of N:N-dimethylhydrazine and stirred for 3 hours at 20 to 25° C. 600 parts of sodium chloride are then added and the whole is stirred for 2 hours longer at 20 to 25° C. The precipitate formed is filtered off and washed with saturated sodium chloride solution and then dried at about 30° C. under reduced pressure.

100 parts of cotton are dyed for 45 minutes at 40° C. in a bath which contains in 2000 parts of water 3 parts of the resulting product and 120 parts of sodium chloride. 30 parts of trisodium phosphate are added and the temperature is kept for another 45 minutes at 40° C. The cotton is then thoroughly rinsed in cold and in hot water

and soaped for 15 minutes at the boil, to yield a deep red dyeing which has good properties of fastness.

Example 36

1.5 parts of the dyestuff of the formula shown in Example 2 are dissolved in 25 parts of boiling water. A dyebath is prepared from this solution in admixture with a solution of 60 parts of sodium chloride in 750 parts of water and 50 parts of cotton yarn are dyed in it for 30 minutes at 40° C. The dyestuff deposited on the fiber is then fixed with addition of 0.04 part of one of the hydrazine compounds of the formulae



and of 15 parts of trisodium phosphate, in the same bath for 1½ hours at 40° C. The yarn is then thoroughly rinsed in cold and in hot water and finally soaped at the boil. A strong red dyeing is obtained.

Example 37

A cotton fabric is impregnated at room temperature with a padding solution which contains in 1000 parts of water

	Parts
Dyestuff mentioned in Example 1	30
Urea	50
Sodium bicarbonate and	20
N:N-dimethylhydrazine	1.5

Without undergoing an intermediate drying the fabric is then steamed for 20 seconds at 120° C. in a high-temperature ager and then finished off in known manner. A blue dyeing is obtained which is fast to washing at the boil and is distinctly stronger than a dyeing produced without adding N:N-dimethylhydrazine.

When the padded fabric is dried before being subjected to the high-temperature steam treatment and N:N-dimethylhydrazine is used, a similar, good result is achieved.

What is claimed is:

1. Process for coloring cellulose fibrous and nitrogenous materials with reactive dyestuff compounds which comprises applying to the fibrous material an aqueous preparation containing a member selected from the group consisting of

(a) a non-quaternized reactive dyestuff compound and a hydrazine compound containing at least one tertiary nitrogen atom, said hydrazine compound being present in an amount of from about 0.1% to about 10% by weight on the weight of the dyestuff.

(b) a reactive dyestuff compound quaternized with a hydrazine compound containing at least one tertiary nitrogen atom.

(c) a non-quaternized reactive dyestuff compound and a reactive dyestuff compound quaternized with a hydrazine compound containing at least one tertiary nitrogen atom.

2. Process for coloring cellulose fibrous and nitrogenous materials with reactive dyestuff compounds which comprises applying to the fibrous material an aqueous preparation containing a member selected from the group consisting of

(a) a non-quaternized reactive dyestuff compound and a hydrazine compound containing at least one tertiary nitrogen atom, said hydrazine compound being present in an amount of from about 0.1% to about 10% by weight on the weight of the dyestuff.

(b) a reactive dyestuff compound quaternized with a hydrazine compound containing at least one tertiary nitrogen atom and

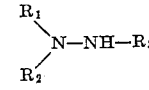
(c) a non-quaternized reactive dyestuff compound and a reactive dyestuff compound quaternized with a hydrazine compound containing at least one tertiary nitrogen atom.

3. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive halogen atom, which comprises applying to the fibrous material an aqueous preparation containing a dyestuff with at least one reactive halogen atom and from about 0.2% to 2% by weight based on the weight of the dyestuff of a hydrazine compound containing at least one tertiary nitrogen atom.

4. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive halogen atom, which comprises applying to the fibrous material an aqueous preparation containing a dyestuff with at least one reactive halogen atom quaternized with a hydrazine compound containing at least one tertiary nitrogen atom.

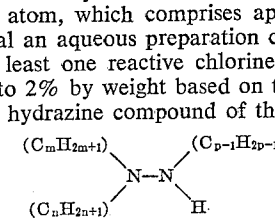
5. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive halogen atom, which comprises applying to the fibrous material an aqueous preparation containing a non-quaternized dyestuff with at least one reactive halogen atom and a dyestuff with at least one reactive halogen atom quaternized with a hydrazine compound containing at least one tertiary nitrogen atom.

6. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing a dyestuff with at least one reactive chlorine atom and from about 0.2% to 2% by weight based on the weight of the dyestuff of a hydrazine compound of the formula



wherein R_1 and R_2 are members selected from the group consisting of alkyl radicals with at most 4 carbon atoms and alkylene members of the same saturated nitrogen-containing, at most six-membered, heterocyclic ring, and R_3 is a member selected from the group consisting of hydrogen and alkyl radicals with at most 4 carbon atoms.

7. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing a dyestuff with at least one reactive chlorine atom and from about 0.2% to 2% by weight based on the weight of the dyestuff of a hydrazine compound of the formula

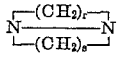


wherein m and n are whole numbers of at most 4 and p is a whole number of at most 5.

8. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fi-

brous material an aqueous preparation containing a dyestuff with at least one reactive chlorine atom and from about 0.2% to 2% by weight based on the weight of the dyestuff of N:N-dimethylhydrazine.

9. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing a dyestuff with at least one reactive chlorine atom and a hydrazine compound of the formula

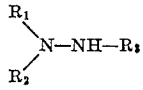


wherein r and s each stands for the whole numbers 3 and 4.

10. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing the dyestuff and from about 0.2% to 2% by weight based on the weight of the dyestuff of 1:5-diaza-bicyclo-(0:3:3)-octane.

11. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing the dyestuff and from about 0.2% to 2% by weight based on the weight of the dyestuff of N-amino-N:N-diaza-bicyclo-(2:2:2)-octane sulfate.

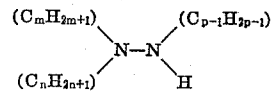
12. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing a nonquaternized dyestuff with at least one reactive chlorine atom and a dyestuff with at least one reactive chlorine atom quaternized with a hydrazine compound of the formula



wherein R_1 and R_2 are members selected from the group consisting of alkyl radicals with at most 4 carbon atoms

and alkylene members of the same saturated nitrogen-containing, at most six-membered, heterocyclic ring, and R_3 is a member selected from the group consisting of hydrogen and alkyl radicals with at most 4 carbon atoms.

13. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing a nonquaternized dyestuff with at least one reactive chlorine atom and a dyestuff with at least one reactive chlorine atom quaternized with a hydrazine compound of the formula



wherein m and n are whole numbers of at most 4 and p is a whole number of at most 5.

14. Process for coloring cellulose fibrous and nitrogenous materials with dyestuffs containing at least one reactive chlorine atom, which comprises applying to the fibrous material an aqueous preparation containing nonquaternized dyestuff with at least one reactive chlorine atom and dyestuff with at least one reactive chlorine atom quaternized with N:N-dimethylhydrazine.

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