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3,334,960

PROCESS FOR COLORING NITROGEN-CONTAINING FIBROUS MATERIAL

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10 Claims. (Cl. 8—54)

This is a continuation-in-part of our application Ser. No. 326,240 filed Nov. 26, 1963, now abandoned. It relates to a process for coloring nitrogen-containing fibrous material.

It has been found that fibrous materials containing nitrogen can be colored, i.e. dyed or printed at room temperature with dyestuffs that are soluble or only dispersible in water in the presence of surface-active assistants by treating the material with an aqueous dye preparation containing 4 to 30% of acid referred to the total weight of the preparation, and finishing off the material so treated by storing it for at least 10 minutes at room temperature and then thoroughly washing and rinsing it.

The dye preparations to be used for the performance of the present invention are of a varying degree of acidity brought about by adding an acid, more especially an organic carboxylic acid to the preparations. Though it is possible to use alternatively inorganic acids, for example phosphoric acid, organic aliphatic monocarboxylic and dicarboxylic acids, above all those of low molecular weight are particularly suitable. Inter alia, good results are obtained by using monochloroacetic or nitric acid. Likewise good results are achieved with tartaric, propionic, glycolic and lactic acid. Particularly good results are obtained with acetic acid and especially with formic acid; these two acids are advantageously used in as concentrated a form as possible. The amount of acid to be added may vary within rather wide limits, for example from 4 to 30% calculated on the weight of the dye preparation, though an amount of the order of 10 to 20% is preferred.

A wide variety of fibrous materials containing nitrogen can be dyed or printed by the present process, including both natural and synthetic materials. Among the natural materials there may be mentioned leathers, pelts (for example sheepskins), hairs, for example human hair, hairs of goats, rabbits or hares, feathers, sisal (which contains proteinic substances embedded in cellulose) and above all wool. Suitable synthetic materials are primarily those from polyacrylonitrile, polyamide (for example condensation products of hexamethylenediamine and adipic acid), polycondensates of ω -aminoundecanoic acid especially of ϵ -caprolactam. It will be readily understood that mixtures containing the afore-mentioned materials may likewise be dyed or printed.

The dye preparation must contain at least one surface-active assistant. These assistants act as levelling, dispersing or wetting agents, may have coacervating power and may be of the non-ionic or cationic kind or even of the anionic type if they have coacervating power. These surface-active agents may be used either alone or in mixtures with one another.

The non-ionic assistants are adducts of ethylene oxide with compounds containing at least one reactive hydrogen atom, that is to say with compounds that contain primary or secondary amino groups or hydroxyl groups, which groups may be linked with a carbonyl group. Thus, the compounds concerned are polyglycol ethers of hydroxy compounds, for example of alkylphenols, such as an octylphenol or nonylphenol, or of higher aliphatic alcohols, such as lauryl, cetyl or octadecyl alcohol, or of

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higher fatty amines containing, for example 10 to 22 carbon atoms.

Among the cationic assistants particularly good results have been obtained with those which owe their solubility in water exclusively to groupings containing a basic nitrogen atom. These compounds are predominantly amine salts or quaternary ammonium salts of cyclic or openchain tertiary amines or of reaction products of alkyloamides of higher fatty acids with alkanolamines. Accordingly, there may be used, for example, cetyl trimethyl ammonium bromide, cetyl pyridinium bromide, a quaternary salt of the reaction product of stearic acid methylolamide with triethanolamine, or a quaternary salt of bis-lauryl-tetramethylethylenediamine. In some cases a particularly advantageous levelling effect may be achieved with combinations of diverse assistants. Particularly suitable combinations are those of two disparate non-ionic assistants such, for example, as adducts of ethylene oxide with higher aliphatic alcohols or with alkylphenols with ethylene oxide adducts of higher aliphatic amines. If desired, there may be used combinations of non-ionic and cationic assistants, the components of such combinations having the structure defined above.

The surface-active coacervating agents may be non-ionic or anionic and must be capable of causing the dye preparation to coacervate. The term coacervation describes the demixing of a colloidal solution of a hydrophilic colloid to form two liquid phases. The phase having a higher content of colloid—in this case the phase containing a larger share of auxiliary—is called the coacervate, whereas the phase having a lower content of colloid—in this case the phase containing less auxiliary—is called the equilibrium liquid. Thus, in a coacervated system the two phases contain the same solvent. It is another characteristic of a coacervated system that a small amount of colloid is capable of taking up a relatively large amount of solvent, in the present case water. As a rule the amount of solvent taken up is a multiple of the amount of coacervating agent used. The two co-existing liquid phases should be present in the form of an emulsion. If necessary, a rather stable emulsion in which the two phases are well distributed can be prepared by adding a thickener.

Auxiliaries capable of satisfying these conditions may belong to a wide variety of compounds. Particularly suitable for the present process are the reaction products obtained from higher fatty acids and hydroxyalkylamines. Ethylene oxide adducts of such reaction products are likewise suitable. Such products can be prepared, without additional use of ethylene oxide, from higher fatty acids, preferably those which contain about 12 carbon atoms such as caprylic, stearic, oleic or especially coconut oil fatty acids, and hydroxyalkyl amines, such as triethanolamine, dihydroxyethylenediamine and preferably diethanol amine. The reaction is so conducted as to produce a molar ratio of hydroxyalkylamine-fatty acid greater than 1, for example 2:1. Such compounds have been described in U.S. Patent No. 2,089,212. If ethylene oxide condensation products of these compounds are required, the molecular proportion of fatty acid to ethylene oxide should be 1:2 to 1:15. The sequence in which the three reactants are reacted is immaterial.

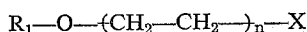
Apart from the reaction products of fatty acids with hydroxyalkylamines there may also be used those from fatty acids with N-substituted or unsubstituted aminoacids or their salts. Such a compound is, for example, the lauric acid sarcoside-monoethanolamine salt.

Furthermore, there may be used as auxiliaries adducts of ethylene oxide with higher fatty acids, higher aliphatic alcohols, alkylphenols, higher alkylmercaptans or higher aliphatic amines. This type of auxiliaries should prefer-

ably contain at most 8 mols of ethylene oxide in the polyglycol ether chain. They correspond to the formula



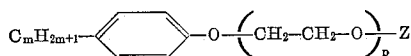
where R represents a hydrophobic radical, X represents a hydrogen atom or an acid solubilizing group and n is a whole number not greater than 8. Special mention in this connection is deserved by the group of compounds of the formula



where n and X have the above meanings and R_1 represents an aliphatic, cycloaliphatic or aliphatic-aromatic radical, preferably a hydrocarbon radical with 10 to 22 carbon atoms. Such radicals are derived from alcohols, such as lauryl, tridecyl, oleyl, octadecyl or hydroabiethyl alcohol, from carboxylic acids such as lauric acid or coconut oil fatty acid, and especially from alkylphenols such as octylphenol or nonylphenol.

These assistants are obtained when the aforementioned alcohols, acids or alkylphenols are reacted with e.g. 1 to 5 mols of ethylene oxide, preferably with 1 to 3 mols of ethylene oxide and the resulting reaction product is, if desired or required, etherified with a halogen-carboxylic or hydroxycarboxylic acid, for example with chloroacetic acid; or is converted into an acid ester with the aid of an organic dicarboxylic acid such as maleic, malonic or succinic acid, or preferably with an inorganic polybasic acid, such as orthophosphoric acid or especially sulfuric acid.

Particularly valuable compounds in this group are those of the formula



where m is a whole number, at least 7, p is a number from 1 to 5, preferably from 1, 2 or 3, and Z represents an acid water-solubilizing group, preferably the radical of a polybasic inorganic acid. It is also possible to use mixtures of assistants of the above formulae, especially those in which the $-(CH_2-CH_2-O)_p-$ radicals are non-uniform so that the average value of n or p no longer represents a whole number, and may be, for example, about 1.5. It is of special advantage to use for the manufacture of the aqueous preparations, instead of the acid ethers or esters, their alkali metal, ammonium or amine salts.

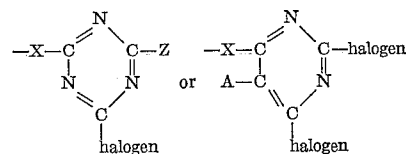
The amounts of coacervating agents to be used may vary within wide limits. Since the amount at which coacervation occurs differs according to the auxiliary used, it is not possible to state generally applicable limiting quantities, but it is a definite advantage if the coacervate formed constitutes at least 10% of the total volume of the dye preparation. The amount of coacervate formed can be measured by sedimentation in a measuring cylinder or according to a microscopic method.

The dyestuffs to be used in the present process are at least dispersible in water, that means that they are water-soluble or only dispersible in water. These dyestuffs may contain reactive groups capable of entering a covalent bond with the fibrous material or they may be free from such groups.

Among the water-soluble dyestuffs preference is given to those which owe their solubility in water to the presence of acid groups, such as carboxylic acid groups, and especially of sulfonic acid groups. In other respects, the dyestuffs may belong to a wide variety of types, for example to the oxazine, triphenylmethane, xanthene, nitro, acridone or phthalocyanine dyestuffs, and above all to the metallized and metal-free monoazo or polyazo dyestuffs or to the anthraquinone dyestuffs.

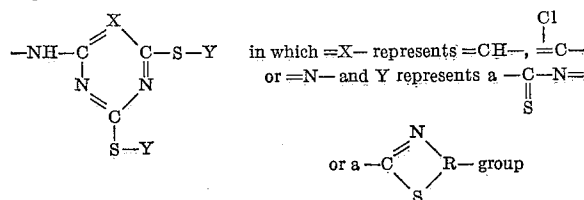
The term "reactive dyestuffs"—which otherwise may belong to the groups mentioned above—includes dyestuffs that are capable of forming a chemical, that is to say covalent, bond with the material to be dyed or printed. As groupings capable of imparting this property

to the dyestuff there may be mentioned epoxide groups, ethyleneimino groups, isocyanate groups, isothiocyanate groups, carbamic acid aryl ester groups, the propiolic acid amide grouping, arylamino groups; groupings that contain a mobile substituent and are easy to split with entrainment of the bond electron 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; above all the vinylacyl groups, such, for example, as the vinylsulfone groups and especially the carboxyvinyl group. These mobile substituents are advantageously in position γ or β of an aliphatic radical which is bound with the dyestuff molecule directly or through an amino, sulfone or sulfonic acid amide group; in the case of those relevant dyestuffs which contain as mobile substituents halogen atoms, these mobile halogen atoms may also be present in an aliphatic acyl radical, for example in an acetyl radical, or in positions β or $\alpha:\beta$ of a propionyl or acryl radical or in a heterocyclic radical, for example in a pyrimidine, pyridazine or triazine ring. The dyestuffs contain advantageously a grouping of the formula



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 represents a hydrogen or halogen atom. The halogen atoms are, for example, bromine atoms, or preferably chlorine atoms.

It is also possible to use dyestuffs containing diphenoxyltriazine groups or those which contain a grouping of the formula



where R stands for an ortho-arylene radical.

Further suitable reactive groupings are the following radicals: Trichloropyridazine, dichloroquinoxaline, dichlorobutene, halogenated pyridazine, sulfonyldichloropropylamide, allylsulfone, allylsulfide, 2-halogenobenzthiazole-carbamide and β -sulfatopropionic acid amide.

Especially favourable results are obtained with reactive dyestuffs that are derived from azo dyestuffs and contain as the reactive group at least one acrylamide or α -halogenoacrylamide group, that is to say an ethylenically unsaturated group, or a group convertible thereinto, for example an $\alpha:\beta$ -dihalogenopropionyl group.

The term "dyestuffs dispersible in water" refers to those which are insoluble in water but are capable of forming in the finely ground state, at least with the aid of a dispersant, very fine aqueous suspensions. In the form of these suspensions the dyestuffs produce very durable dyeings, more especially on synthetic fibers and pelts. It is advantageous to use so-called disperse dyestuffs, which may be free from metal or contain metal bound in complex union.

Preferred azo dyestuffs are those which contain sulfonic acid groups and have affinity for wool, for example from an acetic acid or sulfuric acid bath. Likewise, very good results are obtained with acid azo-chromium complex dyestuffs containing one atomic production of chromium for every dyestuff molecule. However, not only metal-

lized dyestuffs are suitable but also those which are subjected to metallization only in the course of the dyeing process. In this connection particularly valuable results have been obtained with ortho: ortho'-dihydroxyazo dyestuffs and with dyestuffs containing ortho-hydroxycarboxy groupings which are conventionally formed in acid dye-baths with metal donors, more especially potassium bichromate, at an elevated temperature. Particularly favorable results are obtained with azo metal complexes containing one atomic proportion of metal for every two dyestuff molecules in the case where coacervating surface-active assistants are used. Especially suitable metal atoms in this connection are chromium and cobalt. These 1:2-metal complexes may be free from the afore-mentioned acid water-solubilizing groups and contain in their place alkylsulfone or sulfonamide groups.

The present process is suitable for coloring fibrous materials containing nitrogen at room temperature. The impregnation with the aqueous preparation can be carried out on a padder, or the fibrous material can be printed, preferably by the slubbing printing method. Best results have been obtained in vigoureux printing.

After the dye preparation has been applied according to the present process to the material to be dyed or printed, the latter is stored for a varying period of time at room temperature, during which it must be ensured that the material does not dry even partially. Consequently, the material must be stored in a closed system, for example in a closed vessel, or it must be wrapped in a plastic foil or in a rubber blanket. For the present purpose "room temperature" signifies the temperature in the room concerned or a temperature that varies only insignificantly therefrom and it is immaterial whether this temperature is high or low. It is taken to be on an average about 20° C.; if it is higher, the storing period is correspondingly shorter, when it is lower, the storing period is correspondingly extended. The minimum storing period is 10 minutes, but it can be advantageously extended, for example up to 24 to 48 hours, especially in the case of medium strong to dark shades.

After having been stored, the material is washed in order to remove any acid residues from the dyed or printed material. The washing operation may be performed with hot or preferably cold washing liquors which, for the purpose of neutralizing the excess acid, contain an alkali metal compound, such, for example, as sodium carbonate or sodium hydroxide or preferably ammonia.

As further constituents the dye preparations may contain thickening agents, provided they are compatible with acids. There are suitable, above all, starch ethers, carboxyalkyl celluloses, especially carboxymethyl cellulose, etherified carbucic acids or compounds having similar effects.

In manufacturing the dye preparations there may be further added a solution promoter, that is to say, as is commonly known, a substance that renders compounds that are practically insoluble in a certain solvent soluble in that particular solvent. As such compounds there are preferably used in the present process derivatives of ethyleneglycol. Particularly suitable for this purpose are polyethyleneglycols of widely varying molecular weights and monomeric glycols etherified with lower alcohols (for example those containing 1 to 4 carbon atoms), more especially ethyleneglycol monoethyl ether.

Furthermore, it has proved advantageous to add an antifoaming agent to the dye preparation, especially when coacervating agents are used; particularly good results have been obtained with silicone based antifoaming agents.

Notwithstanding the relatively high acid concentrations the fibers are not damaged when treated according to the present process. This is why it offers the advantage that

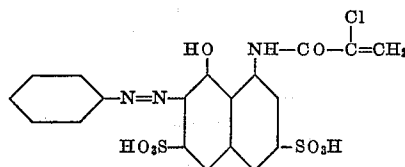
dyeings of considerable tinctorial strength can be achieved without using external heating and more especially also on materials that are sensitive to heat.

Unless otherwise indicated, parts and percentages in the following example are by weight.

Example 1

Pure wool gabardine piecegoods are impregnated in the triangular interspace between the rollers of a horizontal padder with the following preparation and then squeezed to a weight increase of 70%:

10 parts of the dyestuff of the formula



5 parts of a reaction product of 100 parts of commercial oleylamine and 113 parts of ethylene oxide

2 parts of an adduct of 8 mols of ethylene oxide with 1 mole of para-tertiary octylphenol

100 parts of a 5% aqueous thickening of etherified carbucic acids

200 parts of 85% formic acid

683 parts of water

1000 parts

The padded material is stored for 6 hours at room temperature while being protected from drying by being wrapped in a polyethylene foil. After storing, the material is rinsed in a conventional washing machine for 15 minutes with cold water and then until neutral with addition of 2 parts of 25% ammonia solution per 1000 parts of water, then once more rinsed in cold water and finally dried. The resulting vivid red dyeing has good properties of wet fastness.

Similarly good results are obtained when the above continuation of assistants is replaced by one of the following combinations

(a) 5 parts of the adduct of 35 mols of ethylene oxide with 1 mol of octadecyl alcohol

5 parts of cetyl pyridinium bromide wherein the second component may be replaced by

5 parts of cetyl trimethyl ammonium bromide or

5 parts of the dibromide of bis-lauryl tetramethylenediamine

(b) 3 parts of the acetate of a condensation product of 1 mol of stearic acid methylolamide and 1 mol of triethanolamine

2 parts of an adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol or by the separate assistants

(c) 5 parts of the reaction product of 100 parts of commercial oleylamine and 113 parts of ethylene oxide

(d) 5 parts of the adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol.

The replacement of formic acid by thioglycollic acid, acetic acid or acrylic acid gives similarly good results.

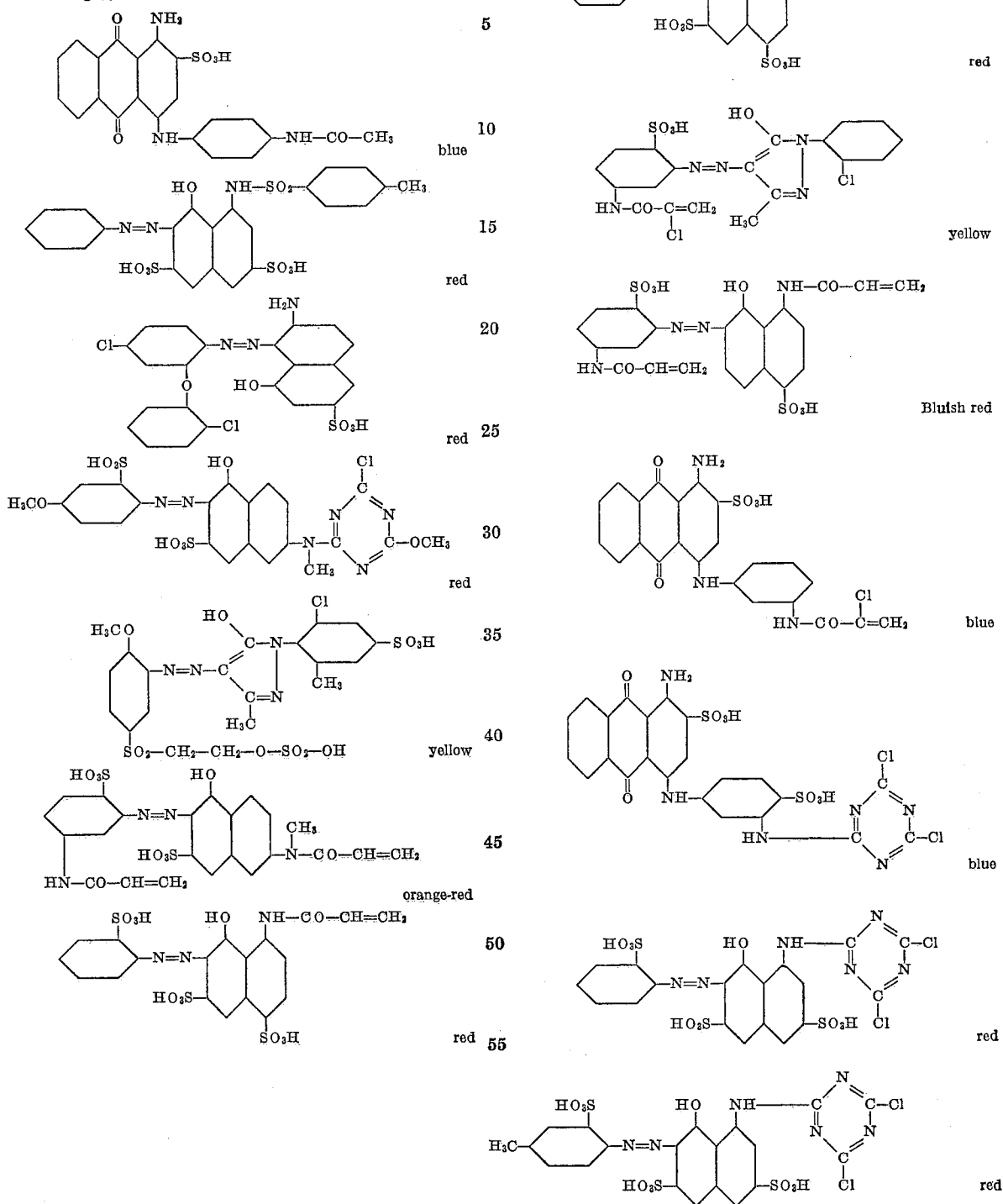
The wool gabardine piecegoods can be replaced by slubbings, loose wool, human hair, feathers, wool felts, ladies dress materials or other woollen fabrics of any quality and state of processing.

Without impairing the results the storing time can be reduced down to 3 hours or extended up to 24 hours.

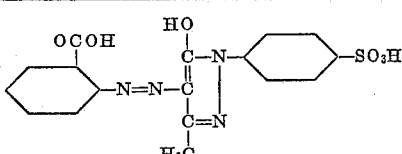
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Example 2

The dyestuff of Example 1 can be replaced by one of the following dyestuffs



1:1-METAL COMPLEXES

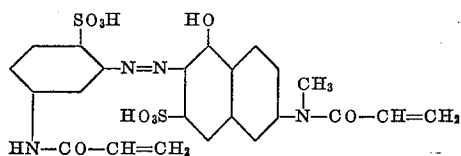
Metal	Dyestuff	Color
Cr		Yellow.

Metal	Dyestuff	Color
Cr		Red.
Cr		Green.
Cr		Blue.
Cr		Blue.

Example 3

Wool muslin is chlorinated and then impregnated with the following padding liquor:

5 parts of the dyestuff of the formula



3 parts of the acetate of a condensation product of 1 mol of stearic acid methylolamide and 1 mol of triethanolamine

2 parts of an adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol

100 parts of a 5% aqueous thickening of etherified carubic acids

150 parts of 85% formic acid

740 parts of water

1000 parts

The padded material is reeled, wrapped up so as to exclude all air and so stored for 20 minutes at room temperature, then thoroughly rinsed in flowing water and finally treated for another 20 minutes in a bath containing per 1000 parts of water 2 parts of sodium carbonate.

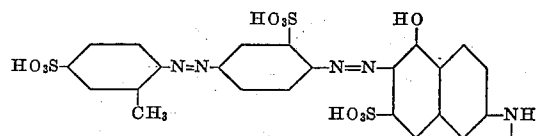
The resulting orange-red dyeing is of medium tinctorial strength and has good wet fastness properties.

Example 4

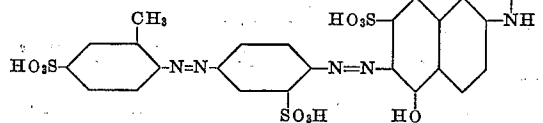
A mixed fabric of equal parts of wool and cotton is padded with the following liquor:

10 parts of the dyestuff of the formula

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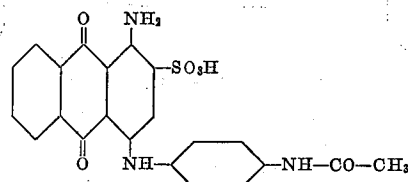


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10 parts of the dyestuff of the formula



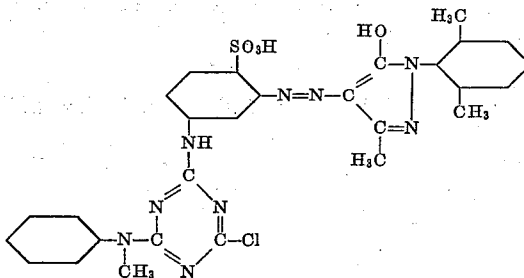
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5 parts of the dyestuff of the formula

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65



70

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3 parts of a reaction product of 100 parts of commercial oleylamine and 113 parts of ethylene oxide
5 parts of an adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol
200 parts of a 5% aqueous thickening of etherified carubic acids

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150 parts of 85% formic acid
617 parts of water

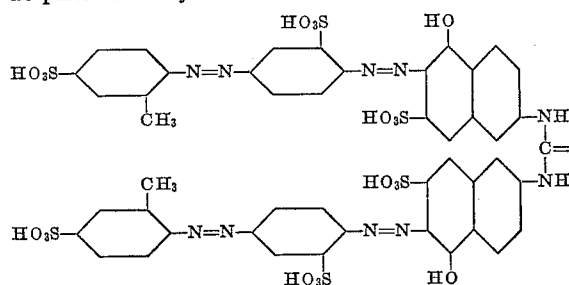
1000 parts

The impregnated fabric is reeled, wrapped in a polyethylene foil and so stored for 10 hours at room temperature, then washed in a bath containing per 1000 parts of water 6 parts of 25% ammonia solution, thoroughly rinsed and finally dried.

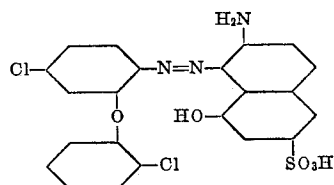
A clear green/red melange effect is obtained, the wool being dyed green and the cotton red.

Equally good results are obtained when the above assistant combination is replaced by 10 parts of dinaphthylmethanesulfonic acid and 50 parts of the reaction product of 1 mol of coconut oil fatty acid with 2 mols of diethanolamine.

When the above dyestuff combination is replaced by 20 parts of the dyestuff of the formula

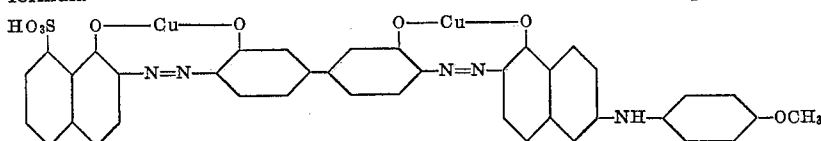


and 10 parts of the dyestuff of the formula

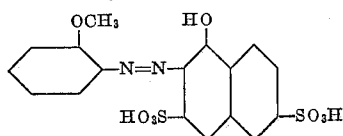


a red tone-in-tone dyeing is obtained.

With a combination of 25 parts of the dyestuff of the formula



and 10 parts of the dyestuff of the formula

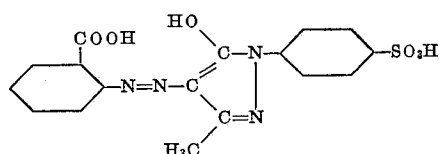


a two-color effect is obtained, wherein the wool is dyed red and the cotton share blue.

Example 5

A sheep skin is impregnated with the following padding liquor by padding or brushing:

10 parts of the 1:1-chromium complex dyestuff containing per 1 atom of chromium 1 molecule of the dyestuff of the formula



5 parts of a reaction product of 100 parts of commercial oleylamine and 113 parts of ethylene oxide

12

2 parts of an adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol

100 parts of a 5% aqueous thickening of etherified carubic acids

5 200 parts of 85% formic acid
683 parts of water

1000 parts

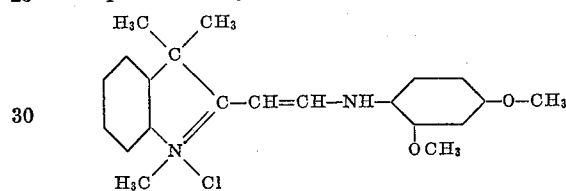
The impregnated skin is stored for 5 hours, and is prevented from drying by being wrapped in a polyethylene foil. After this storing the skin is thoroughly rinsed in a bath containing per 1000 parts of water 3 parts of 25% ammonia solution, then washed neutral, once more rinsed and finally dried.

15 The skin is dyed a full yellow shade. Chrome-tanned leather can be dyed in a similar manner.

Example 6

A fabric of which the fibers consist predominantly of a copolymer of acrylonitrile and vinyl acetate is impregnated on a two-roller padder and then expressed to a weight increase of about 70%. The padding liquor consists of:

20 10 parts of the dyestuff of the formula



30 5 parts of a reaction product of 100 parts of commercial oleylamine and 113 parts of ethylene oxide

35 5 parts of an adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol

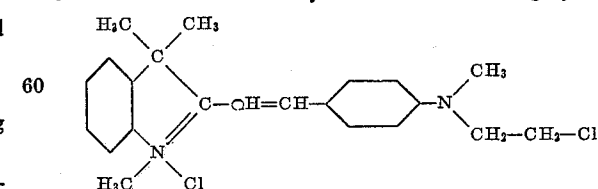
100 parts of a 5% aqueous thickening of etherified carubic acids

40 200 parts of 85% formic acid
680 parts of water

1000 parts

50 The impregnated fabric is wrapped in a polyethylene foil and stored for 10 hours at room temperature, then washed neutral in a full-width washing machine in a bath containing per 1000 parts of water 8 parts of 25% ammonia solution, thoroughly rinsed and then dried.

55 A vivid yellow dyeing is obtained. Instead of the dyestuff used above there may be used the following dyestuff



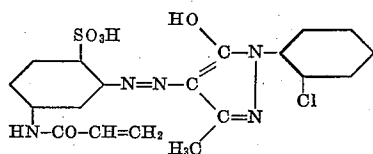
60 Similar results are obtained when the assistant combination is replaced by 40 parts of the reaction product of 1 mol of coconut oil fatty acid with 2 mols of diethanolamine.

Example 7

70 A fabric consisting of continuous polyamide fibers of the polycondensate of adipic acid and hexamethylenediamine is impregnated on a two-roller padder with the following liquor:

75 10 parts of the dyestuff of the formula

13



2 parts of an adduct of 8 mols of ethylene oxide with
1 mol of para-tertiary octylphenol
10 parts of etherified carubic acids
200 parts of 85% formic acid
778 parts of water

1000 parts

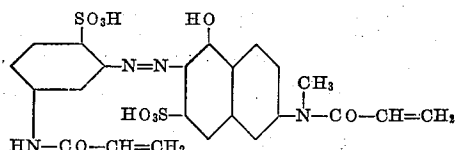
The impregnated fabric is wrapped in a polyethylene foil and stored for 10 hours at room temperature while being gently rotated. The fabric is then thoroughly rinsed in a full-width washing machine and finally dried.

A strong yellow shade is obtained. Similar results are obtained with continuous fiber fabrics from ϵ -caprolactam, or staple fiber fabrics from hexamethylene diamine adipate or from ϵ -caprolactam.

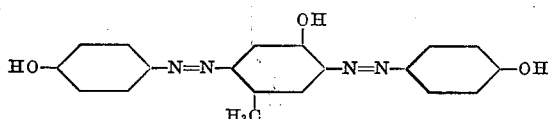
Example 8

A mixed fabric consisting of equal parts of wool and polyamide fibers (obtained by polycondensation of adipic acid and hexamethylene diamine) is impregnated on a two-roller padder with a liquor of the following composition:

5 parts of the dyestuff of the formula



5 parts of the dyestuff of the formula



10 parts of an adduct of 8 mols of ethylene oxide with
1 mol of para-tertiary octylphenol
5 parts of etherified carubic acids
200 parts of 85% formic acid
775 parts of water

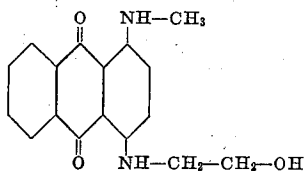
1000 parts

The impregnated fabric is stored for 14 hours at room temperature while being gently rotated, then washed neutral in a full-width washing machine in a bath containing per 1000 parts of water 8 parts of 25% ammonia solution, thoroughly rinsed and then dried.

The mixed fabric is dyed a tone-in-tone orange red.

When the dyestuff combination used above is replaced by the following combination:

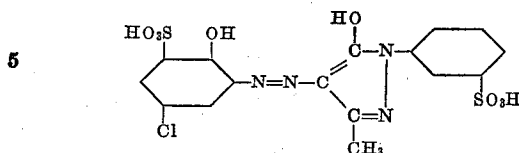
10 parts of the dyestuff of the formula



10 parts of the 1:1-chromium complex dyestuff con-

14

taining per atom of chromium 1 molecule of the dyestuff of the formula

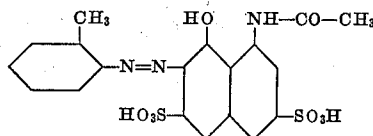


10 a clear blue-red two-tone effect is obtained, the wool being dyed red and the polyamide fiber blue.

Example 9

A fabric of real silk is impregnated on a padder and expressed to a weight increase of 70%. The padding liquor has the following composition:

10 parts of the dyestuff of the formula



5 parts of a reaction product of 100 parts of commercial oleylamine and 113 parts of ethylene oxide

2 parts of an adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol

300 parts of a 5% aqueous thickening of etherified carubic acids

200 parts of 85% formic acid

483 parts of water

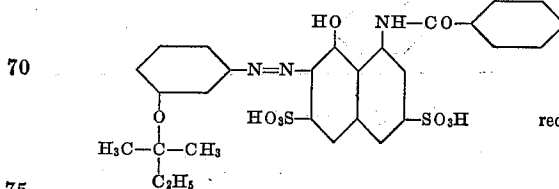
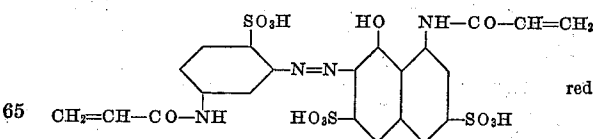
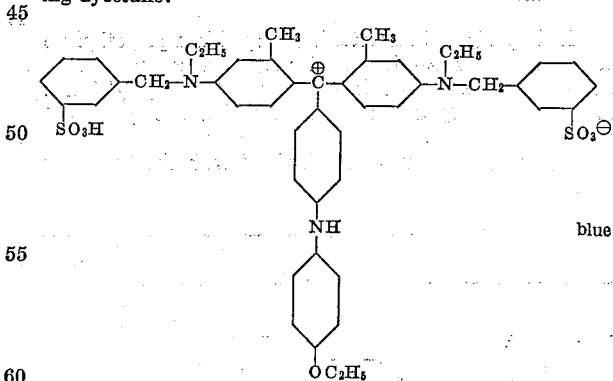
1000 parts

The impregnated fabric is reeled, wrapped in a polyethylene foil and stored for 16 hours at room temperature, and then thoroughly rinsed in cold water.

The resulting red dyeing has good properties of fastness.

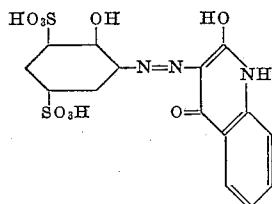
The assistant combination can be replaced by 30 parts of the reaction product of 1 mol of coconut oil fatty acid with 2 mols of diethanolamine without impairing the quality of the dyeing.

Similar, good results are achieved by using the following dyestuffs:



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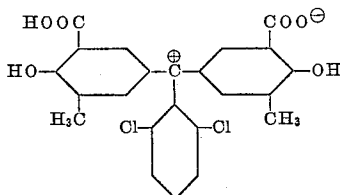
1:1-copper complex containing for every atom of chromium 1 molecule of the dyestuff of the formula



Example 10

Pure wool gabardine piecegoods are impregnated on a horizontal two-roller padder and then expressed to a weight increase of 70%. The padding liquor used consists of:

20 parts of the dyestuff of the formula



- 15 parts of a commercial starch ether
- 200 parts of 85% formic acid
- 20 parts of preparation from
- 65 parts of water
- 60 parts of an adduct of 8 mols of ethylene oxide with 1 mol of para-tertiary octylphenol
- 25 parts of a reaction product from
- 100 parts of commercial oleylamine and
- 113 parts of ethylene oxide
- 10 parts of potassium bichromate
- 735 parts of water

1000 parts

The impregnated material is wrapped in a polyethylene foil, stored for 24 hours at room temperature, then neutralised in an ammoniacal bath and thoroughly rinsed. A vivid blue dyeing is obtained which has good wet fastness properties.

Similar, good results are obtained with the following dyestuffs

	Shade
	Red.
	Black.

Example 11

A pure woollen, non-woven garment felt is impregnated on a two-roll padder at room temperature with the follow-

16

ing preparation and then squeezed to a weight increase of 80%:

10 parts of the metal complex dyestuff containing 1 atom of cobalt for each mol of the following 2 dyestuffs:

5

red

10

and

15

20

25

30

35

40

45

50

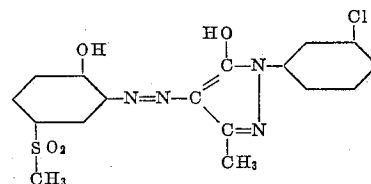
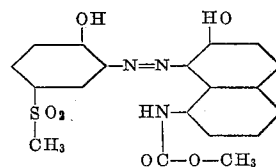
55

60

65

70

75

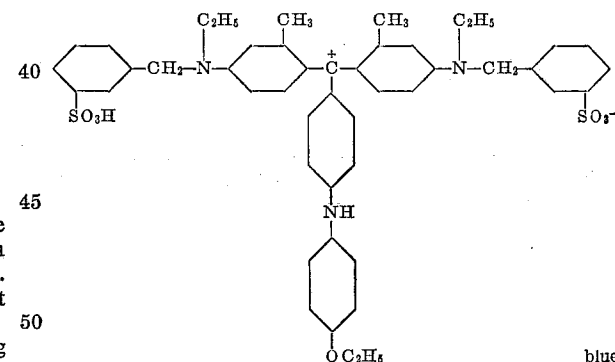


40 parts of a reaction product from 1 mol of coconut oil fatty acid with 2 mols of diethanolamine, 100 parts of a 5% aqueous thickening of etherified carubic acids,

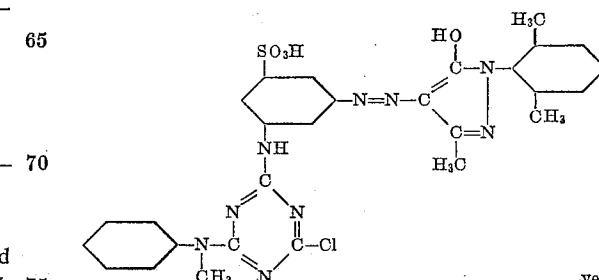
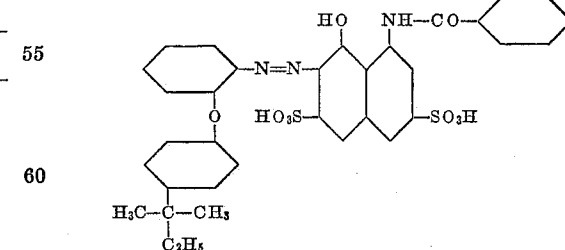
200 parts of formic acid of 85% strength and 650 parts water.

The padded felt is reeled, wrapped airtight in a polyethylene film and stored for 48 hours at room temperature. After having been so stored the felt is thoroughly rinsed with cold water on a full-width washing machine and then dried. The resulting strong brown shade has good properties of fastness.

Similar results are obtained with any dyestuff enumerated in the tables of Example 2 or with the following dyestuffs:



blue



yellow

1:2-METAL COMPLEXES

Metal	dyestuff molecules	color
Cr		Orange red.
Cr		Green.
Co		Green.
Cr		Orange red.
Cr		Brown.
Cr		Red.
Cr		Blue.

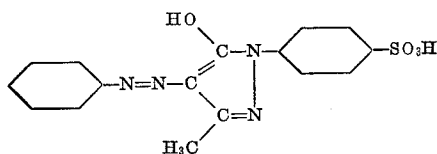
Similar good results are obtained when the garment felt is replaced by worsted tops and the padder is replaced by a Vigoureux printing machine.

Similar good results are also obtained when only 100 parts of formic acid are used.

19 Example 12

Pure woollen ladies' dress material is impregnated on a two-roll padder with the following preparation and then squeezed to a weight increase of 80%.

5 parts of the dyestuff of the formula



40 parts of a reaction product from 1 mol of coconut oil fatty acid and 2 mols of diethanolamine

100 parts of a 5% aqueous thickener of etherified carubic acids

2 parts of a silicone based anti-foaming agent

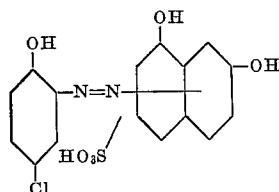
200 parts of formic acid of 85% strength, and

653 parts of water.

The padded fabric is reeled, wrapped airtight in a rubber foil and stored for 24 hours at room temperature, and then finished off as described in Example 1. A level, orange-red dyeing is obtained.

If the 100 parts of thickener used above are replaced by water, similar good results are obtained. The storing time may be reduced to 20 minutes without substantially impairing the quality of the dyeing.

If the above dyestuff is replaced by 20 parts of the dyestuff of the formula



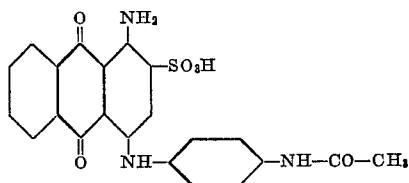
the fabric is stored and then reeled on a winch and thoroughly rinsed, then treated for 30 minutes in a boiling 1% aqueous bath of potassium dichromate (referred to the dry weight of the goods) and the dyeing is finished off by rinsing, a fast grey shade is obtained.

Instead of the woollen fabric a sheepskin can be dyed, and in this case the impregnation is advantageously performed by brushing. In otherwise identical manner a perfect dyeing results which may require a slight after-tanning depending on the tanning method original used.

Example 13

A so-called stretch fabric for ski clothes, whose weft consists of wool and the warp of crimped continuous polyamide filaments from a hexamethylenediamine adipate condensate, is impregnated on a 3-roll padder with the following preparation and then squeezed to a weight increase of 100%:

10 parts of the dyestuff of the formula



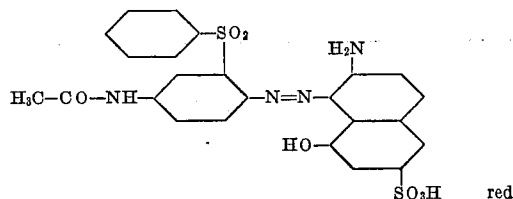
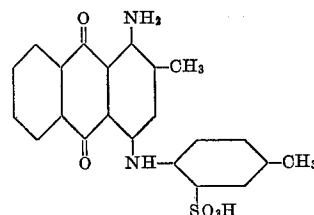
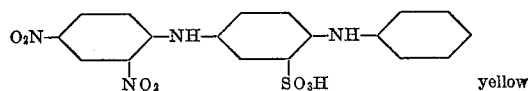
40 parts of a 63% solution of the diethanolamine salt of coconut oil fatty acid, coconut oil fatty acid-polyethyleneglycol ester with 6-8 mols of ethylene oxide sodium tetralinsulphonate in aqueous isopropanol

100 parts of a 5% aqueous thickener from etherified carubic acids
2 parts of a silicone based anti-foaming agent
200 parts of formic acid of 85% strength and
648 parts of water.

20

The padded material is reeled, wrapped airtight in a rubber blanket and stored for 24 hours at room temperature. The fabric is then rinsed in cold water, washed for 20 minutes in a cold bath containing in 1000 parts of water 1 part of ammonia and 0.5 part of the reaction product of 1 mol of coconut oil fatty acid with 2 mols of diethanolamine and finally once more rinsed. A deep blue tone-in-tone dyeing is obtained.

Similar results are obtained when the following dyestuffs are used:



Equally good results are also obtained when the 40 parts of the auxiliary combination described above are replaced by an equal quantity of one of the following auxiliaries:

(a) Reaction product of 1 mol of coconut oil fatty acid with 2 mols of diethanolamine;

(b) Condensation product of 1 mol of para-tertiary nonylphenol with 5-6 mols of ethylene oxide;

(c) Mixture of equal parts of coconut oil fatty acid diethanolamine salt and coconut oil fatty acid-polyethyleneglycol ester with 6-8 mols of ethylene oxide;

(d) Lauric acid sarcoside-monoethanolamine salt, or

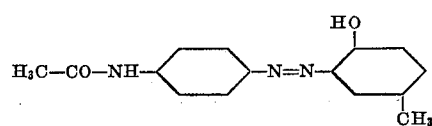
(e) 44% aqueous solution of the ammonium salt of the acid sulphuric acid ester of the condensation product from 1 mol of para-tertiary nonylphenol with 2 mols of ethylene oxide.

When instead of the wool/polyamide mixed weave a knitwear article from wool and basically modified polypropylene fibres is treated, similar good results are achieved.

Example 14

A carpet having a jute backing and a pile of textured polyamide from ϵ -caprolactam is impregnated by immersing it twice on a 3-roll padder in the following preparation:

20 parts of the dyestuff of the formula



30 parts of a condensation product from para-tertiary nonylphenol and 5 mols of ethylene oxide

40 parts of a 5% aqueous thickening from etherified carubic acids

2 parts of a silicone based anti-foaming agent
200 parts of formic acid of 85% strength and
708 parts of water.

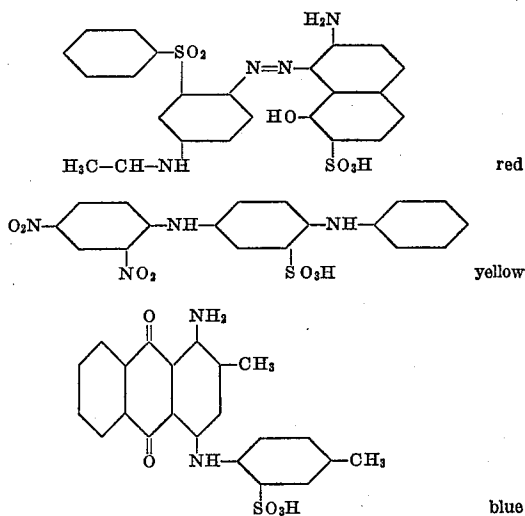
The impregnated carpet is squeezed to a weight increase of 80%, rolled up, wrapped airtight and stored for 24

hours at room temperature while being slowly rotated.

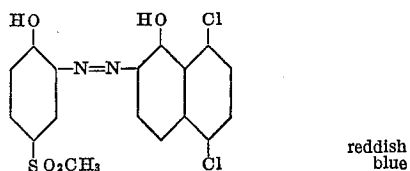
The carpet is then thoroughly rinsed in cold water and washed for 15 minutes in a bath maintained at 30° C. which contains for every 1000 parts of water 1 part of sodium carbonate and 1 part of heptadecenyl benzimidazole sulphionate.

Finally, the carpet is once more rinsed and then dried. It is dyed a strong yellow shade, while the jute backing is only faintly dyed.

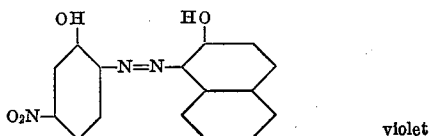
Similar results are obtained with the auxiliaries used in Examples 1 to 4 and the following dyestuffs:



Metal complex dyestuff containing 1 atom of chromium for every 2 mols of the dyestuff of the formula



Metal complex dyestuff containing 1 atom of cobalt for every 2 mols of dyestuff of the formula



What is claimed is:

1. In a process for coloring fibrous materials containing nitrogen at room temperature with dyestuffs that are at least dispersible in water in the presence of at least one surfactant selected from the group consisting of nonionic ethylene oxide condensation products, cationic compounds containing a quaternary nitrogen atom and nonionic and anionic coacervating agent, the improvement which comprises bringing the material to be colored into contact with an aqueous preparation consisting substantially of 4 to 30%, calculated on the total weight of the preparation and 100% strength acid, of an aliphatic carboxylic acid with at most 5 carbon atoms then storing the material so treated for at least 10 minutes during which time the material is prevented from drying whereupon it is finished off by being washed.

2. In a process for coloring according to claim 1 the improvement which comprises applying to the fibrous material an aqueous preparation containing an aliphatic carboxylic acid selected from the group consisting of formic acid and acetic acid.

3. In a process for coloring according to claim 1 the improvement which comprises applying to the fibrous material an aqueous preparation containing a combination of two non-ionic surfactants one of which is a condensation product of ethylene oxide with a fatty amine containing 10 to 22 carbon atoms and the other is a condensation product of ethylene oxide with an aryl phenol containing 6 to 12 carbon atoms in the alkyl radical.

4. In a process for coloring according to claim 1 the improvement which comprises applying to the fibrous material an aqueous preparation of a two-phase system produced by a coacervating surfactant that is a reaction product of a higher fatty acid with hydroxyalkyl amines.

5. In a process for coloring according to claim 1 the improvement which comprises applying to the fibrous material an aqueous preparation of a two-phase system produced by a coacervating surfactant of the formula



wherein R is a hydrophobic radical, X represents a member selected from the group consisting of hydrogen and an acid solubilizing group and n is a whole number from 1 to 8.

6. In a process for coloring according to claim 1 the improvement which comprises applying to the fibrous material an aqueous preparation consisting of a coacervated two-phase system wherein the coacervate constitutes at least 10% by volume of the whole preparation.

7. In a process for coloring according to claim 1 the improvement which comprises applying to wool an aqueous preparation containing at least one water-soluble 1:1-metal complex azo dyestuff and a combination of two non-ionic surfactants one of which is a condensation product of ethylene oxide with a fatty amine containing 10 to 22 carbon atoms and the other is a condensation product of ethylene oxide with an alkyl phenol containing 6 to 12 carbon atoms in the alkyl radical.

8. In a process for coloring according to claim 1 the improvement which comprises applying to wool an aqueous preparation containing at least one water-soluble metal-free acid wool dyestuff and a combination of two non-ionic surfactants one of which is a condensation product of ethylene oxide with a fatty amine containing 10 to 22 carbon atoms and the other is a condensation product of ethylene oxide with an alkyl phenol containing 6 to 12 carbon atoms in the alkyl radical.

9. In a process for coloring according to claim 1 the improvement which comprises applying to wool an aqueous preparation of a coacervated two-phase system wherein the two-phase system is formed by a coacervating surfactant selected from the group consisting of a reaction product of a higher fatty acid with hydroxyalkyl amines and a compound of the formula



wherein R is a hydrophobic radical, X represents a member selected from the group consisting of hydrogen and an acid solubilizing group and n is a whole number from 1 to 8 and contains at least one dyestuff selected from the group consisting of a water-soluble 1:1-metal complex azo dyestuff and a water-soluble metal-free acid wool dyestuff.

10. In a process for coloring according to claim 1 the improvement which comprises applying to wool an aqueous preparation of a coacervated two-phase system wherein the two-phase system is formed by a coacervating surfactant selected from the group consisting of a reaction product of a higher fatty acid with hydroxyalkyl amines and a compound of the formula



wherein R is a hydrophobic radical, X represents a member selected from the group consisting of hydrogen and an acid solubilizing group and n is a whole number from

1 to 8 and contains at least one water-soluble 1:2-metal complex azo dyestuff.

References Cited

UNITED STATES PATENTS

2,089,212	8/1937	Kritchevsky	-----	8—87	X
2,999,731	9/1961	Harding	-----	8—54	
3,043,650	7/1962	Wegmann et al.	-----	8—1.23	
3,104,931	9/1963	Casty et al.	-----	8—54	
3,208,990	9/1965	Benz et al.	-----	8—55	X
3,223,470	12/1965	Boedeker et al.	-----	8—54	X

FOREIGN PATENTS

238,540 4/1962 Australia.

OTHER REFERENCES

- 5 B. Kramrisch: Review of Textile Progress, vol. 12, 1960, pp. 365-367.
 Casty: Amer. Dyestuff Reporter, Dec. 12, 1960, pp. 105-117.
- 10 NORMAN G. TORCHIN, *Primary Examiner*.
 T. J. HERBERT, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,334,960

August 8, 1967

Heinz Abel

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 21, line 62, for "agent" read -- agents --; column 22, line 7, for "aryl" read -- alkyl --.

Signed and sealed this 6th day of August 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents