United States Patent Office 3,071,427 Patented Jan. 1, 1963

3,071,427

PROCESS FOR DYEING NITROGENOUS FIBERS AND PREPARATIONS FOR CARRYING OUT THE PROCESS

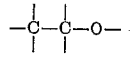
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No Drawing. Filed Apr. 23, 1959, Ser. No. 808,312
Claims priority, application Switzerland Apr. 30, 1958
10 Claims. (Cl. 8—22)

For dyeing nitrogenous fibers, especially wool, hitherto only two classes of metalliferous dyestuffs have acquired any substantial importance, namely, 1:1-chromium complexes of monoazo-dyestuffs containing sulfonic acid groups, and 1:2-chromium or cobalt complexes of azo-dyestuffs, usually monoazo-dyestuffs, in which the complex molecule (hereinafter referred to simply as "the complex") contains in the two azo-dyestuff molecules, which take part in the formation of the complex and may be identical or different from one another, a total of at most a single sulfonic acid group or advantageously no free sulfonic acid group and also no free carboxylic acid group, that is to say, one that does not take part in the formation of the complex, and instead usually sulfonic acid amide groups or similar substituents, such as sulfone groups or sulfonic acid ester groups.

1:2-complexes containing in the molecule more than one acid group imparting solubility in water, for example, two or more sulfonic acid groups, have hitherto proved to be almost useless. They yield from strongly acid as well as weakly acid baths on wool not only extremely unlevel, skippery dyeings, but also weak tints, since, even when a large excess of dyestuff is used, a certain relatively low strength of dyeing cannot be exceeded and, for example, the production of the especially desirable dark brown, navy blue and black tints is very difficult. Useful to very valuable dyeings of any desired strength and satisfactory levelness and good properties of fastness can, however, be obtained by producing the aforesaid complexes on the fiber or in some cases during the dyeing operation from the metal-free dyestuffs and suitable agents yielding metal. It will therefore be easily understood that this procedure, namely the after-chroming process or single bath chroming process, is still finding extensive use even though it is attended by substantial technical disadvantages and difficulties and noticeable damage to the wool cannot be avoided.

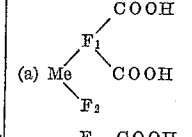
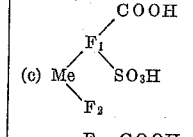
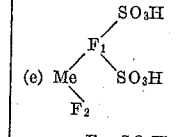
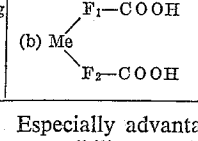
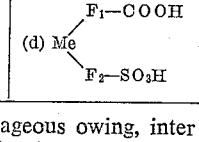
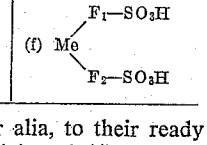
The process of this invention enables nitrogenous fibers, especially wool, to be dyed uniformly and in any desired strengths in a very simple manner with 1:2-complexes of the kind referred to above which have hitherto been unusable for this purpose. In this process for dyeing nitrogenous fibers capable of being dyed with acid dyestuffs, the fibers are dyed in an aqueous bath with a dyestuff consisting substantially of a 1:2-chromium or cobalt complex compound of an azo-dyestuff, which compound contains at least two acid groups imparting solubility in water, and the dyeing operation carried out in the presence of a compound which contains at least one basic nitrogen atom to which is bound at least one radical containing a polyglycol ether chain, and which compound contains at least three



groups and at least four carbon atoms not belonging to such groups.

By the process of this invention nitrogenous fibers can be dyed which are capable of being dyed in the usual manner with acid dyestuffs, for example, silk, polyamide fibers of ε-caprolactam or of adipic acid and hexamethylene diamine. The process is especially advantageous for dyeing wool, if desired, in admixture with other nitrogenous fibers or fibers free from nitrogen. The process is advantageous for dyeing polyamide fibers inasmuch as those fibers can be dyed the same shade as wool, whereas the after-chroming of polyamide fibers often leads to shades which are substantially the same as those of the unchromed dyestuffs, or shades on wool which are considerably different from the shades on polyamide fibers.

As dyestuffs there are used 1:2-chromium or cobalt complex compounds of azo-dyestuffs, for example, disazo-dyestuffs or more especially monoazo-dyestuffs, that is to say, complexes in which two molecules of an azo-dyestuff or one molecule each of two different azo-dyestuffs are bound in complex union to one atom of chromium or cobalt. The complex may contain, for example, a disazo-dyestuff and a monoazo-dyestuff or preferably two identical or different monoazo-dyestuff molecules. Furthermore, the complex must contain at least two acid groups imparting solubility in water, that is to say, free carboxylic acid groups (—COO-cation) or especially free sulfonic acid groups (—SO_3-cation), a carboxylic acid group taking part in the formation of the complex not being included as a group imparting solubility in water, because, when bound in this manner, it no longer imparts solubility in water. The groups imparting solubility in water may be distributed in any way within the complex. As a rule it is of advantage that at least one sulfonic acid group be present. When the complex contains a total of two groups imparting solubility in water and the complex-forming metal is represented by Me and the two dyestuffs by F_1 and F_2, the possibilities may be represented as follows:

	2—COOH	1—COOH+1—SO_3H	2—SO_3H
One dyestuff contains two groups imparting solubility and the other dyestuff is free from groups imparting solubility.	 (a)	 (c)	 (e)
The two dyestuffs each contain one group imparting solubility.	 (b)	 (d)	 (f)

Especially advantageous owing, inter alia, to their ready accessibility are the dyestuffs under (*e*) and (*f*), namely those which contain two sulfonic acid groups in the molecule of the dyestuff complex, or more generally dyestuffs which contain at least two sulfonic acid groups in the molecule of the complex, those dyestuffs being preferred in which, as in the complexes under (*f*), there are present two monoazo-dyestuff molecules each of which contains at least one sulfonic acid group and which are bound in complex union to one atom of chromium or cobalt.

Apart from the inevitable difference between F_1 and F_2 in the complexes (*a*), (*c*), (*d*) and (*e*), the dyestuffs F_1 and F_2 may in all cases be of the same or different constitution. The positions of the groups imparting solubility in water in the dyestuffs F_1 and F_2 is optional. They may be present in the radical of the diazo-component or coupling component and, if desired, two to four such groups may be present in the same radical.

Too large a number of groups imparting solubility in water, especially sulfonic acid groups, is usually inadvisable, especially in the case of dyestuffs of relatively low molecular weight, because the properties of wet fastness of the dyeings may be reduced thereby. The presence of two to four sulfonic acid groups in the complex has been found to be especially advantageous.

As groupings capable of forming metal complexes the monoazo-dyestuffs advantageously contain ortho:ortho'-dihydroxy-azo groupings or ortho-hydroxy-ortho'-carboxy-azo-groupings. However, other complex-forming-groupings may be present, such as ortho-hydroxy-ortho'-carboxymethoxy-groupings or ortho-hydroxy-ortho'-amino-azo groupings.

The azo-dyestuffs required for making the metal complexes can be obtained by the usual known methods and from known diazo components and coupling components. A great many azo-dyestuffs of this kind have been known for a long time as chrome dyestuffs. There are used for making such azo-dyestuffs, for example, as diazo-components ortho-hydroxy- or ortho-carboxyamines of the benzene or naphthalene series and as coupling components hydroxybenzenes, hydroxynaphthalenes, 2:4-dihydroxy-quinolines, pyrazolones and acetoacetylamino-benzenes capable of coupling in a position vicinal to a hydroxyl group (or an enolizable keto group).

In this connection there may be mentioned the following components:

(1) Diazo-components free from groups imparting solubility in water (including, as will be understood, ortho-aminocarboxylic acids free from further groups imparting solubility in water).

(2) Diazo-components containing groups imparting solubility in water.

(3) Coupling components free from groups imparting solubility in water.

(4) Coupling components containing groups imparting solubility in water.

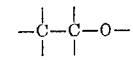
The 1:2-complexes to be used in the process of this invention can be obtained by the usual known methods from the metal-free monoazo-dyestuffs, advantageously by the known methods for making 1:2-metal complexes free from groups imparting solubility in water. In the production of symmetrical complexes, in which the metal atom is bound to two identical dyestuff molecules, it is of advantage to treat the dyestuff in such manner and with such an agent yielding metal, such as an alkali metal chromosalicylate, chromium acetate, sodium cobalt tartrate, cobalt acetate or cobalt sulfate, that the desired complex is obtained directly. In this connection there may also be mentioned chroming with an alkali metal bichromate in the presence of a reducing agent.

For making asymmetrical complexes another method is generally desirable in order to obtain unitary products instead of mixtures containing a substantial amount of symmetrical by-products some of which contain no groups imparting solubility in water and are therefore undesired. In this case it is of advantage to prepare the 1:1-chromium complex of one of the two dyestuffs to be used for making the asymmetrical 1:2-complex, advantageously the dyestuff which contains at least one group imparting solubility in water, provided that this does not apply to both dyestuffs, and then to react the 1:1-chromium complex with the other metal-free dyestuff. It should be mentioned that for making the 1:1-complex as well as the 1:2-complex of ortho:ortho'-dihydroxy-azo-dyestuffs not only the ortho:ortho'-dihydroxy-azo-dyestuff itself can be used, but also

the corresponding ortho-hydroxy-ortho'-alkoxy-azo-dyestuff. For the direct production of 1:2-complexes, and especially for making the 1:1-complexes to be converted into the 1:2-complexes, there may therefore be used, instead of ortho-hydroxy-diazo-compounds, the corresponding ortho-alkoxy-diazo-compounds, especially the methoxy-compounds.

The working up of the 1:2-complexes may in some circumstances involve certain difficulties, because these compounds are very soluble in water. Complexes, which for this reason cannot be salted out, can be isolated by evaporating the reaction mixture or by other means, for example, by the addition of certain organic solvents that are miscible with water.

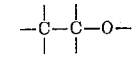
The nitrogenous compounds, in the presence of which the process of this invention is carried out, contain at least one basic nitrogen atom to which at least one radical containing a glycol ether chain is bound. This chain consists of at least two units of the formula



and may be bound directly or through a bridge member, for example, an alkylene radical, such as the radical

$$—CH_2—CH_2—CH_2—$$

to the nitrogen atom. The molecule of the nitrogenous compound must contain at least three



advantageously

$$—CH_2—CH_2—O—$$

groups.

Furthermore, the nitrogenous compounds must contain at least four carbon atoms not belonging to such groups. Thus, they advantageously contain at least one aliphatic or alicyclic radical having at least 8 carbon atoms bound to one another, and advantageously an aliphatic radical having at least 12 carbon atoms bound to one another, and also an aromatic radical containing an aliphatic side chain and bound by an aryl carbon atom to the basic nitrogen atom.

From the foregoing statements it will be understood there are advantageously used as nitrogenous compounds in the process of this invention reaction products of at least three molecular proportions of an α:β-alkylene oxide per molecular proportion of organic compound which contains at least one basic primary or secondary amino group or a basic tertiary amino group and also an alcoholic hydroxyl group, and salts thereof or quaternary ammonium salts derived therefrom.

As starting materials for making the aforesaid reaction products there are used α:β-alkylene oxides, such as ethylene oxide, propylene oxide or glycide. Especially valuable products are obtained from ethylene oxide.

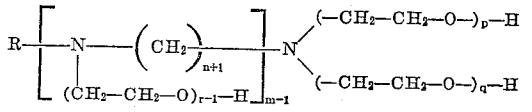
As organic compounds which contain at least one basic primary or secondary amino group or one basic tertiary amino group and an alcoholic hydroxyl group, there may be mentioned amines of the aliphatic, aromatic or alicyclic series. Among those of the aliphatic series there may be mentioned monamines, for example, diethylamine, butylamine, hexylamine, dodecylamine, cetylamine, oleylamine, octadecylamine, arachidylamine, behenylamine or mixtures of these monamines, or polyamines such as propylene diamine, triethylene tetramine or the corresponding N-alkyl-polyamines having alkyl radicals of high molecular weight containing 8–2 carbon atoms. There may also be mentioned basic derivatives of such amines, such as esters of hydroxy-amines with higher fatty acids, for example, the triethanolamine ester of coconut oil fatty acid, or partial amides of polyamines with fatty acids, for example, triethylene tetramine monoacylated with coconut oil fatty acid. Among amines of the aromatic series there may be mentioned more especially amines of the benzene and naphthalene series having alkyl side

chains containing, for example, 8–18 carbon atoms. Among amines of the alicyclic series there are advantageously used resin amines, such as abietylamine, abietylmethylamine, the mixture of amines corresponding to tall oil which contains resin amines in addition to higher alkylamines, or hydrogenated abietylamine. There may also be used as starting materials amidines, such as lauric acid amidine or stearic acid amidine.

For the process of this invention there are suitable products obtainable by the reaction of one molecular proportion of an amine with at least three molecular proportions, for example, 3–20 molecular proportions, or more than 20 molecular proportions, of an alkylene oxide, for example, the reaction product of one mol of dodecylamine with about 6 mols of ethylene oxide, or of one mol of oleylamine with 6, 8 or 16 mols of ethylene oxide, or of one mol of octadecylamine with 4, 8 or 16 mols of ethylene oxide, the reaction product of a monoalkyl-propylene diamine, of which the alkyl radical corresponds to the radical of tallow fatty acids, with 8 mols of ethylene oxide, the reaction product of a monoalkl-propylene diamine of which the alkyl radical is unbalanced and contains 16–18 carbon atoms, with 6 mols of ethylene oxide.

From the above statements it will be apparent that nitrogenous compounds of the formula

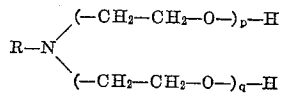
(1)



are especially suitable for the process, in which formula R represents an advantageously unbranched aliphatic hydrocarbon radical containing at least 12, and advantageously 16–22, carbon atoms, m and n each represent the whole number 1 or 2, and p, q and r reach represent a whole number such that the sum of $p+q+(m-1)(r-1)$ is at least 3 and advantageously 8 to 20.

It is also apparent that there are especially suitable for the process nitrogenous compounds of the formula

(2)



in which R represents an advantageously unbranched aliphatic hydrocarbon radical containing at least 12, and advantageously 16–20, carbon atoms, and p and q each represent a whole number such that the sum of $p+q$ is at least 3 and advantageously 8 to 20.

Instead of compounds containing fre hydroxyalkyl groups there may be used acid esters thereof with polybasic acids, for example, phosphoric acid or sulfuric acid, or water-soluble salts of these esters, for example, alkali metal salts or salts with ammonia or amines.

The ethylene oxide addition products can be made by the methods customary for making such products. For example, they can be made by reacting the components with the aid of heat. Advantageously the alkylene oxide is not added to the amine all at once but gradually, by introducing the alkylene oxide, for example, in the gaseous or liquid state into the amino-compound at a temperature at which the alkylene oxide reacts, for example, at 50° C. to 200° C. If desired the reaction may be carried out in a closed vessel under superatmospheric pressure, advantageously at 2–10 atmospheres gauge pressure. The reaction mixture may, if necessary, contain a catalyst. As catalysts there may be used with advantage substances of alkaline reaction, such as metallic sodium, alkali metal hydroxides, alkali metal carbonates or salts of alkali metals with carboxylic acids of low molecular weight.

The condensation products used in the process of the invention are soluble or easily dispersible in water. The solubility in water may be increased, if desired, by introducing groups that enhance the solubility in water. Thus, for example, quaternary ammonium salts may be used which contain alkylene glycol chains derived from $\alpha:\beta$-alkylene oxides and are obtained, for example, by the additive combination of alkylating agents with reaction products of primary, secondary or tertiary amines of the kind mentioned above with alkylene oxides. There may be mentioned quaternary ammonium salts obtained by quaternating with dimethylsulfate the reaction product of oleylamine with 6–10 mols of ethylene oxide.

Instead of the reaction products of alkylene oxides with primary or secondary or tertiary amines of the kind mentioned above there may be used products obtained by introducing polyglycol ether chains having an appropriate number of ether groups into the amines.

The process of this invention is suitable for dyeing proper, as well as for printing. In dyeing from aqueous baths the proportion of the substances to be added to the dyebaths may vary within relatively wide limits. The proportion of dyestuff depends, of course, on the strength of the dyeing desired. It will of course be understood that mixtures of complexes of the aforesaid constitution may be used and also minor proportions, that is to say, up to 20% of the total dyestuff, of dyestuffs of different constitution, especially so-called shading dyestuffs. It is desirable to adjust the proportion of the nitrogenous compound relatively to that of the dyestuff so that this ratio is about 1:8 to 1:2. It is of advantage to add the nitrogenous compound in a proportion amounting to one quarter of the quantity of dyestuff. The proportion of the nitrogenous compound should amount to at least 0.2 percent (calculated on the weight of the fiber) even when pale dyeings are desired for which less than one percent of dyestuff is used calculated on the weight of the fiber.

Furthermore it is of advantage to carry out the dyeing operation in an acid to at most neutral medium, so that the pH value of the dyebath is within the range of about 3–7 and advantageously 3–5. This pH value can be achieved with advantage by the addition of acetic acid or an ammonium salt or a mixture of these substances. There may be used, for example, 3–8 parts of acetic acid of 40% strength or 2–5 parts of ammonium sulfate or ammonium acetate for every 100 parts of fibrous material. It is also of advantage to add sodium sulfate or sodium acetate to the dyebath.

As is customary in dyeing nitrogenous fibers, especially wool, dyeing is carried out at a raised temperature, for example, by starting the dyeing process proper at about 50–80° C., heating the bath to the boiling temperature and continuing and completing the dyeing at that temperature. However, in the process of this invention, even for dyeing wool, it is not essential to bring the temperature very close to or precisely at the boiling point of the dyebath. Almost equally good results are obtained by carrying out the process at a temperature decidedly below the boiling temperature, for example at a temperature within the range of 80–90° C. In order to ensure that the action of the nitrogenous compound is effective at the outset, the acid, if desired, sodium sulfate, and also the assistant, that is to say, the nitrogenous compound may be incorporated in the bath at room temperature or at most a slightly higher temperature, and if desired also the material to be dyed, and the bath is then heated and the dyestuff added to the bath in the form of an aqueous solution only when the bath is hot.

If desired, the dyeing may be carried out by a continuous method, for example, by first padding the material in the cold with a neutral dyestuff solution and then subjecting it to a short after-treatment in a hot acid bath.

The present process is also very suitable for printing worsted tops by the slubbing method. The printing pastes required for this purpose contain, in addition to at least one dyestuff and an assistant of the specified kind, a thickening agent such as tragacanth or British gum, and

they should further contain an acid, such as acetic acid. They may also contain further additives conventionally incorporated with printing pastes, such as oil of turpentine, hydrotropic agents such as urea and/or substances that inhibit reduction, such as sodium nitrobenzenesulfonate.

In other respects the process may follow the practice conventionally used in slubbing printing. The printed material is steamed, for example under atmospheric pressure, advantageously with at least one interruption, for 40 to 120 minutes.

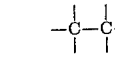
The resulting slubbing print is distinguished by a good tinctorial yield and very good properties of fastness, more especially by good fastness to potting and acid cross-dyeing.

The wet-fastness properties of the prints obtained by the present process can be distinctly improved insofar as bleeding is concerned when, after the fibers have absorbed the desired amount of dyestuff from an acid bath (that is to say at a pH value below 6), the pH value of the dyebath is raised above 6. This can be achieved quite generally with any water-soluble compound of alkaline reaction. In order, however, to prevent damage to the fiber—more especially in the case of wool dyeing—it is of advantage to add a substance of alkaline reaction of which even a certain excess is incapable of raising the pH value to more than about 9, and it is particularly advantageously with a nitrogenous base, for example an amine such as an ethanolamine. In most cases good results are obtained with ammonia, and above all with hexamethylenetetramine. The orthophosphates, polyphosphates or bicarbonates of alkali metals likewise produce good results.

The treatment at a raised pH value requires relatively little time, for example about 10 to 30 minutes, and it is advantageously performed at the same temperature as the dyeing. For example, the dyebath can be maintained at the boil during the after-treatment, or the temperature may be allowed to drop slightly for example by stopping the supply of external heat after the pH value has been raised. Finally, the dyeings can be rinsed in warm and/or cold water and then dried in the usual manner.

For dyeing mixtures of nitrogenous fibers and cellulose fibers, for example so-called half-wool, the increasing of the pH value is particularly advantageous in that it admits of working by a two-stage, single-bath process. First the wool share of the blended fiber is dyed as described above, with the cellulose share remaining practically undyed. After raising the pH value (for example with the aid of ammonia) sodium sulfate and then a direct-dyeing cotton dyestuff are added, preferably without further heating. Particularly suitable dyestuffs are those which at most dye wool only very slightly even at temperatures in the neighborhood of 100° C. The material is then dyed until the cellulose fiber has likewise assumed the desired tint, for example for half an hour, and then finished in the usual manner. To improve the wet fastness properties of the cellulose fiber share it may be of advantage to carry out a conventional after-treatment with an agent capable of improving the wet fastness, for example with a condensation product of dicyandiamide and formaldehyde.

Instead of entering the dyestuff and the nitrogenous compound separately in the dyebath to be used in the present process, these two constituents, and, if desired, further substances, may be made up into stable preparations ready for use. These preparations likewise form an object of the present invention; they are characterized in that they contain as dyestuff substantially a 1:2-chromium or 1:2-cobalt complex of a monoazo dyestuff, the molecule of said complex containing at least two acid groups capable of imparting solubility in water, and further contain a compound with at least one basic nitrogen atom to which is bound at least one radical containing a polyglycol ether chain, and the molecule contains at least 3



groups and at least four carbon atoms that do not form part of such a group.

These preparations can be made by mixing the dyestuff complex with the nitrogenous compound of the specified kind, or by evaporating or atomizing a solution or suspension that contains the dyestuff and the assistant. Whether and to what extent this involves the formation of a bond, for example a salt-like bond, between dyestuff and assistant is immaterial since the preparation produces the same tinctorial result as when the components are added separately to the dyebath.

EXAMPLE 1

100 parts of knitting wool are immersed at 50 to 80° C. in a dyebath containing in 3000 parts of water, 10 parts of crystalline sodium sulfate, 6 parts of acetic acid of 40% strength, 0.5 part of the addition product of oleylamine and ethylene oxide (described below sub A) and 2 parts of the dyestuff described sub B. In the course of ½ hour the bath is raised to the boil, and dyeing is performed for 1 hour at the boil. The wool is then rinsed and dried. A level, greyish blue dyeing is obtained. When the ethylene oxide addition product is omitted, a very skittery, greyish dyeing of no practical value is obtained.

When the dyestuff described sub B is replaced by the 1:2-chromium complex obtained in identical manner from the monoazo dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene, a slightly more reddish, likewise level dyeing is obtained. In this case the dyebath, after immersion of the wool, may be raised to 85° C. only instead of to the boil, dyeing being continued at this temperature for 1 hour.

A. *Manufacture of the Addition Product of Ethylene Oxide*

100 parts of commercial oleylamine are mixed with 1 part of finely divided sodium, the mixture is heated to 140° C., and ethylene oxide is then introduced at 135 to 140° C. When the ethylene oxide is being absorbed rapidly, the reaction temperature is lowered to 120 to 125° C. and the introduction of ethylene oxide is continued until 113 parts thereof have been absorbed. The reaction product obtained in this manner gives an almost clear solution in water.

B. *Manufacture of the Dyestuff*

41.6 parts of the monoazo dyestuff obtained by coupling diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid with 1-hydroxynaphthalene are dissolved in 1000 parts of water and mixed with 100 parts by volume of a solution of sodium chromosalicylate containing 2.85% of chromium. Refluxing for several hours completes the metallization. The chromium complex is salted out with sodium chloride, filtered off and dried.

EXAMPLE 2

Wool is dyed as described in Example 1 with the cobalt complex prepared as described below. A level olive dyeing results. When the addition of the ethylene oxide addition product is omitted, a skittery, weak grey dyeing is obtained.

The cobalt complex is prepared in the following manner:

43.3 parts (0.1 mol) of the dyestuff from diazotized 4:6-dinitro-2-amino-1-hydroxybenzene and 1-aminonaphthalene-4-sulfonic acid, in the form of a paste of about 30% strength, are stirred with 1000 parts of hot water to form a homogeneous slurry. 100 parts by volume of 2 N-sodium hydroxide solution are added, and the mixture is raised to 75° C. Only part of the dyestuff is dis-

solved. This suspension is treated with a solution of 16.9 parts of crystalline cobalt sulfate (0.06 mol) in 50 parts of hot water. After a short time, the dyestuff has passed completely into solution. The reaction mixture is stirred for 1 hour at 75 to 80° C. The cobaltiferous dyestuff is precipitated from this solution with 100 parts by volume of 2 N-acetic acid and 100 parts of sodium chloride, filtered off and dried.

EXAMPLE 3

The procedure is identical with that described in Example 1, except that the under-mentioned chromium complex is used. A level red dyeing is obtained, whereas the identical procedure but without addition of the ethylene oxide addition product, gives a weak, skittery dyeing.

The chromium complex is prepared in the following manner:

A solution of 51.0 parts of the dyestuff prepared by coupling diazotized 4-chloro-2-amino-1-hydroxybenzene-6-sulfonic acid with 1-phenyl-3-methyl-5-pyrazolone-4'-sulfonic acid in 750 parts of water is rendered slightly alkaline to pheno'phthalein by adding sodium hydroxide. 93 parts by volume of a solution of sodium chromosalicylate containing 2.85% of chromium are added and the whole is refluxed with stirring until the parent dyestuff can no longer be detected. The deep-red solution is neutralized with acetic acid and evaporated to dryness.

EXAMPLE 4

When wool is dyed as described in Example 1, except that the under-mentioned chromium complex is used, a strong navy blue dyeing is obtained. When the ethylene oxide addition product is omitted, a skittery violet-grey dyeing is obtained.

The chromium complex is prepared in the following manner:

0.01 mol of the chromium complex, containing 1 atom of chromium bound in complex union to 1 molecule of dyestuff, of the dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene-8-sulfonic acid is refluxed for 2 hours with 0.01 mol of the dyestuff from diazotized 4-ch'oro-2-amino-1-hydroxybenzene and 5:8-dichloro-1-hydroxynaphthalene in 200 cc. of water with the addition of 20 cc. of 2 N-sodium carbonate solution. The reaction mixture is then evaporated to dryness under reduced pressure.

EXAMPLE 5

A dye preparation is made from the 1:2-chromium complex in which one atom of chromium is bound in complex union to one molecule of the dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene and one molecule of the dyestuff from the same diazo compound a 1-hydroxy-5:8-dichloronaphthalene, and the ethylene oxide addition product described in Example 1 sub A, by evaporating or atomizing an aqueous solution containing these two ingredients. It is of advantage to make the preparation, as described hereinafter, immediately following upon the manufacture of the chromium complex without intermediate isolation of the complex.

100 parts of wool tops, 2000 parts of water and 4 parts of acetic acid of 40% strength are heated to 60° C. A solution of 3 parts of the dye preparation in a small amount of water is added. Within ½ hour the whole is raised to the boil and dyeing is continued for 1 hour at the boil. The dyeing is then rinsed and dried. A level, full bluish grey dyeing results. The same complex yields skittery, weaker and duller dyeings when the ethylene oxide addition product is omitted.

The dye preparation can be made in the following manner:

0.01 mol of the chromium complex, containing 1 atom of chromium bound in complex union to 1 molecule of dyestuff, of the dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene is heated with 0.01 mol of the dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 5:8-dichloro-1-hydroxynaphthalene in 300 cc. of water with the addition of 20 cc. of 2 N-sodium hydroxide solution, to 90° C. and maintained for 2 hours at 90 to 95° C. with stirring. 2.0 grams of the ethylene oxide addition product prepared as described sub A in Example 1 are added, and the whole is neutralized with acetic acid and, if desired after the addition of British gum, evaporated to dryness under reduced pressure.

EXAMPLE 6

A dye preparation is produced (advantageously as described hereinbelow) from the ethylene oxide addition product described sub A in Example 1 and the 1:2-cobalt complex of the dyestuff from diazotized 4-chloro-2-amino-1-hydroxybenzene-6-sulfonic acid and 2-hydroxynaphthalene-6-sulfonic acid. Wool is dyed with this preparation as described in Example 5. A full dyeing of a very pure violet tint results.

The dye preparation can be manufactured as follows:

25 parts by volume of 2 N-sodium hydroxide solution are added to a suspension of 10.05 parts of the disodium salt of the dyestuff from diazotized 4-chloro-2-amino-1-hydroxybenzene-6-sulfonic acid and 2-hydroxynaphthalene-6-sulfonic acid in 200 parts of water. The whole is heated to 80° C. while being stirred, and 20 parts by volume of a cobalt sulfate solution containing 3.25% of cobalt are added. When the metallization is complete, the solution is treated with 4 parts of the ethylene oxide addition product described sub A in Example 1. The mixture is then neutralized with acetic acid and dried in an atomizing drier.

Instead of with the dye preparation described in the preceding paragraph the dyeing according to the method described in the first paragraph of this example can be carried out with either of the following preparations:

I. 0.01 mol of the chromium complex, containing 1 atom of chromium bound in complex union to 1 molecule of dyestuff, of the dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone is heated with 0.01 mol of the dyestuff from diazotized 4-chloro-2-amino-1-hydroxybenzene-6-sulfonic acid and 5-pyrazolone-3-carboxylic acid in 300 cc. of water with addition of 20 cc. of 2 N-sodium hydroxide solution, to 90° C. and stirred for several hours at 90 to 95° C. On completion of the complex formation 3.5 grams of the ethylene oxide addition product sub A in Example 1 are added, the clear solution is adjusted with acetic acid to pH=7 and evaporated under reduced pressure. This preparation dyes wool very pure bluish red tints.

II. 0.01 mol of the chromium complex, containing 1 atom chromium bound in complex union to 1 molecule of dyestuff, of the dyestuff from diazotized 5-nitro-2-amino-1-hydroxybenzene and 2-aminonaphthalene-6-sulfonic acid is heated for several hours at 90 to 95° C. with 0.01 mol of the dyestuff from diazotized 4-chloro-2-amino-1-hydroxybenzene-6-sulfonic acid and 5:8-dichloro-1-hydroxynaphthalene in 300 cc. of water with addition of 20 cc. of 2 N-sodium hydroxide solution. When the starting materials can no longer be detected, the solution is treated with 4 grams of the ethylene oxide addition product described sub A in Example 1, neutralized with acetic acid and evaporated to dryness. When used for dyeing by the usual method in an acetic acid bath, this dyestuff dyes wool a very level, bluish gray.

EXAMPLE 7

The chromium complex described below is used for dyeing by the method of Example 1. In this manner a full red dyeing is obtained.

When the ethylene oxide addition product is omitted, only a weak, skittery, practically useless dyeing is obtained.

The chromium complex is obtained in the following manner:

100 parts by volume of sodium chromosalicylate containing 2.85% of chromium are added to a solution of 39.9 parts of the monoazo dyestuff from diazotized 4-chloro-2-amino-1-hydroxy-benzene-6-sulfonic acid and 5-pyrazolone-3-carboxylic acid in 800 parts of water. When, after having refluxed for several hours, starting material can no longer be detected, the deep red solution is neutralized with acetic acid and evaporated to dryness under reduced pressure.

EXAMPLE 8

The method described in Example 1 is used, except that the assistant prepared as described sub A in Example 1 is replaced by one of the ethylene oxide addition products described hereinbelow; this procedure likewise yields level dyeings:

(*a*) N-alkyl-propylenediamine (whose alkyl radical corresponds to the radicals of tallow fatty acid)+8 mols of ethylene oxide,

(*b*) N-alkyl-propylenediamine (whose alkyl radicals are unbranched and saturated and contain 16 to 18 carbon atoms)+6 mols of ethylene oxide,

(*c*) Mixture of behenylamine and arachidylamine+8–20 mols of ethylene oxide,

(*d*) Mixture of the amines obtained by reduction of tallow fatty acid amides+6–8 mols of ethylene oxide,

(*e*) N-dodecyl-propylenediamine+6 mols of ethylene oxide,

(*f*) Dodecylamine+3 mols of ethylene oxide,

(*g*) Dodecylamine+3 mols of propylene oxide. This propylene oxide addition product is prepared as follows: 24 parts of commercial dodecylamine are heated to 160° C. in the presence of 0.13 part of finely dispersed sodium in a current of nitrogen, and gaseous propylene oxide is then introduced until 19.5 parts thereof have been absorbed;

(*h*) The acid sulfuric acid ester obtained as described below:

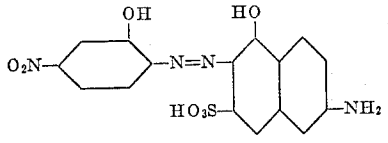
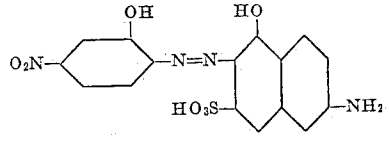
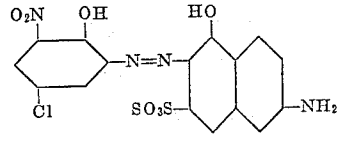
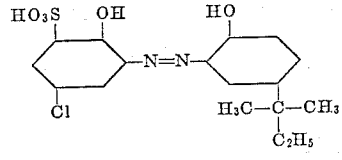
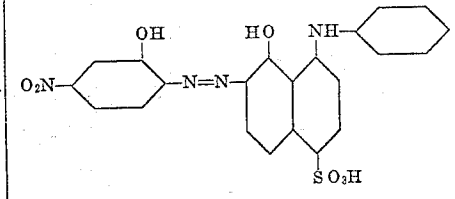
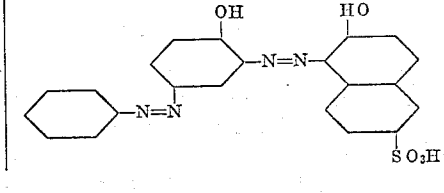
79 parts of a mixture of fatty amines (0.3 mol) consisting of 30% of hexadecylamine, 25% of octadecylamine and 45% of octadecenylamine are reacted in the presence of 0.8 part of sodium with ethylene oxide until 106 parts (2.4 mols) of the latter have been absorbed. The reaction temperature is in the beginning 140 to 150° C. and can be gradually lowered to 120 to 125° C. 30.75 parts (0.05 mol) of the resulting ethylene oxide addition product are then mixed in a stirring flask at 60° C. within 15 minutes with 5.4 parts of urea and then within 30 minutes with 5.4 parts of sulfamic acid (0.05 mol+10%) and maintained for 5 to 6 hours under nitrogen on a boiling water-bath. The resulting product (41 parts) is readily water-soluble and of neutral reaction.

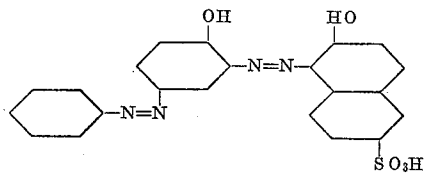
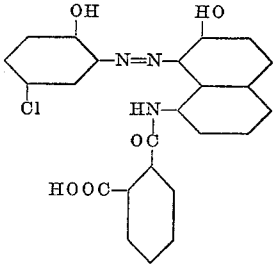
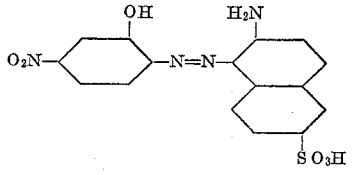
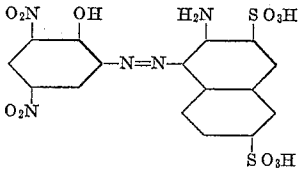
EXAMPLE 9

The procedure is as described in Example 1, except that the chromiferous dyestuff used in that example is replaced by one of the 1:2-metal complexes described below which can be prepared in the usual manner. Level dyeings are thus likewise obtained.

In Table A are listed 1:2-complexes in which one atom of metal is bound in complex union to 2 molecules of the same dyestuff.

TABLE A

	Metal	Dyestuff	Tint on wool
1	Cr		Bluish black.
2	Co		Blue.
3	Cr		Navy blue.
4	Cr		Brown.
5	Cr		Green.
6	Cr		Olive-brown.

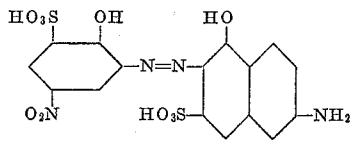
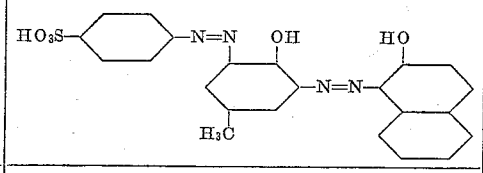
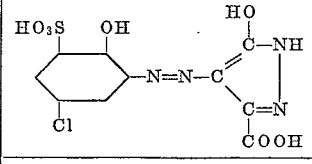
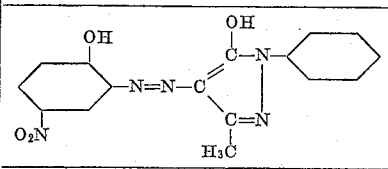
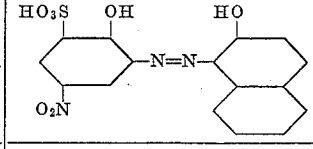
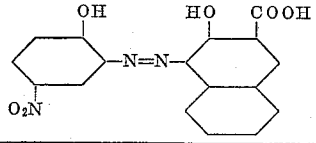
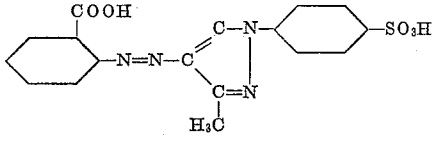
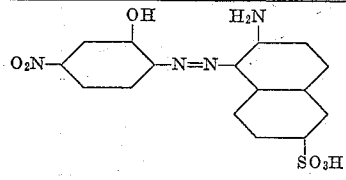
	Metal	Dyestuff	Tint on wool
7	Co		Reddish brown.
8	Cr		Greenish grey.
9	Co		Blue.
10	Cr		Olive.

In Table B are listed 1:2-complexes in which 1 atom of metal is bound in complex union to 1 molecule each of two different dyestuffs.

EXAMPLE 10

A dyebath is prepared from 4000 parts of water, 3 parts of acetic acid of 40% strength, 0.25 part of the ethylene

TABLE B

	Metal	1st dyestuff	2nd dyestuff	Tint on Wool
1	Cr			Bluish grey.
2	Cr			Red.
3	Cr			Blackish brown.
4	Cr			Green.

oxide addition product described sub A in Example 1, and 1 part of the 1:2-chromium complex of the monoazo dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone. A mixed weave consisting of 80% of wool and 20% of polyamide fibers (nylon) is immered in this bath at 50° C. The bath is raised to the boil within 45 minutes and dyeing is continued for 1 hour at the boil. A red dyeing is obtained in which both fibers display substantially identical tints.

By using as dyestuff the 1:2-chromium complex of the monoazo dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 2-hydroxynaphthalene, a greyish blue dyeing is obtained which is likewise level.

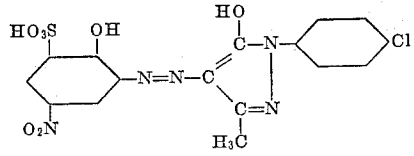
EXAMPLE 11

100 parts of woolen piece goods are immersed at 60° C. in a dyebath containing in 4000 parts of water 5 parts of acetic acid of 40% strength, 10 parts of crystalline sodium sulfate, 0.25 part of the ethylene oxide addition product according to Example 1 and 1 part of the 1:2-chromium complex of the monoazo dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone. The whole is raised within ½ hour to the boil and dyeing at the boil is continued for 1 hour. The heating is discontinued and 3 parts of aqueous ammonia of 25% strength are added. After 15 minutes the wool is removed from the dyebath, immediately rinsed in water and dried. A level red dyeing is obtained which has much better wet fastness properties than when the subsequent addition of ammonia is omitted. The addition of ammonia raises the pH value from about 5.0 to 8.0.

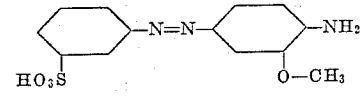
Instead of with ammonia the raising of the pH value towards the end of the dyeing operation can be achieved with hexamethylenetetramine, triethanolamine or sodium bicarbonate.

EXAMPLE 12

A dyebath is prepared from 5000 parts of water, 0.5 part of the assistant described sub A in Example 1, 5 parts of acetic acid of 40% strength and 0.5 part of the 1:2-chromium complex of the dyestuff of the formula



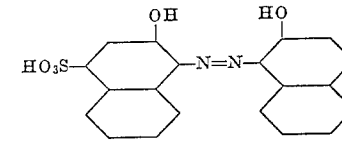
100 parts of a fabric consisting of equal parts of wool and viscose rayon staple fibers are immersed in this dyebath at 50° C. The temperature is raised within 20 minutes to 85° C., maintained for 20 minutes at 85° C., then raised to the boil, and dyeing is continued at the boil for ½ hour. The heating is then discontinued and 3 parts of ammonia of 25% strength are added; by then the pH value should have reached about 8. After 10 minutes 1 part of the dyestuff is added which has been obtained by condensing the monoazo dyestuff of the formula



in the molecular ratio of 1:2 under superatmospheric pressure and in the presence of sodium hydroxide with 4:4'-dinitrostilbene-2:2'-disulfonic acid and oxidizing the resulting product with sodium hypochlorite. After another 10 minutes 20 parts of crystalline sodium sulfate are added. Dyeing at the boil is continued for ½ hour, and the fabric is rinsed in cold water and dried. An orange dyeing is obtained in which the two types of fibers are dyed approximately identical tints.

EXAMPLE 13

With the 1:2-chromium complex of the dyestuff of the formula



a printing paste is prepared which contains:

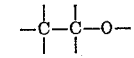
20 parts of dyestuff,
50 parts of urea,
180 parts of tragacanth thickening 60:1000,
25 parts of the ethylene oxide addition product described sub A in Example 1,
30 parts of acetic acid of 40% strength,
20 parts of oil of turpentine,
675 parts of water,
1000 parts.

Wool tops are subjected to a conventional slubbing printing process with this paste. The printed wool is then steamed twice for 45 minutes on each occasion under atmospheric pressure, rinsed in water containing per liter 2 cc. of ammonia of 25% strength and then in plain water, and finished in the conventional manner.

The resulting greyish blue slubbing print is much stronger than one obtained in identical manner except for the omission of the ethylene oxide addition product.

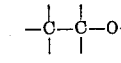
What is claimed is:

1. A process for dyeing nitrogenous fibers capable of being dyed with acid dyestuffs, which comprises treating the fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two acid groups imparting solubility in water, and carrying out the treatment in the presence of a compound which contains at least one basic nitrogen atom to which is bound at least one radical containing a polyglycol ether chain, the molecule containing at least 3



groups and at least 4 carbon atoms not belonging to such group.

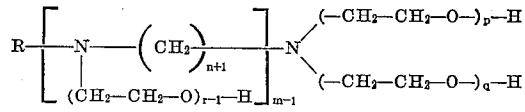
2. A process for dyeing wool, which comprises treating the wool fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two acid groups imparting solubility in water, and carrying out the treatment in the presence of a compound which contains at least one basic nitrogen atom to which is bound at least one radical containing a polyglycol ether chain, the molecule containing at least 3



groups and at least 4 carbon atoms not belonging to such group.

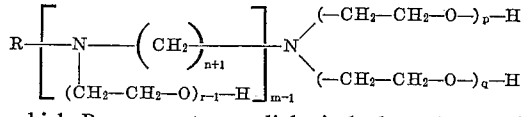
3. A process for dyeing wool, which comprises treating the wool fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two acid groups imparting solubility in water, and

carrying out the treatment in the presence of a compound which corresponds to the formula



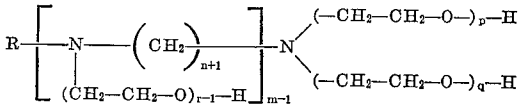
in which R represents an aliphatic hydrocarbon radical containing from 12 to 22 carbon atoms, *m*, *n*, *p*, *q* and *r* each represent a whole number, *m* and *n* being at the most 2 and the sum $p+q+(m-1)(r-1)$ being at least 3 and at the most 20.

4. A process for dyeing wool, which comprises treating the wool fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two sulfonic acid groups, and carrying out the treatment in the presence of a compound which corresponds to the formula



in which R represents an aliphatic hydrocarbon radical containing from 12 to 22 carbon atoms, *m*, *o*, *p*, *q* and *r* each represent a whole number, *m* and *n* being at the most 2 and the sum $p+q+(m-1)(r-1)$ being at least 3 and at the most 20.

5. A process for dyeing wool, which comprises treating the wool fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains, bound to one molecule of the complex forming metal, two molecules of a monoazo dyestuff containing at least one sulfonic acid group, and carrying out the treatment in the presence of a compound which corresponds to the formula

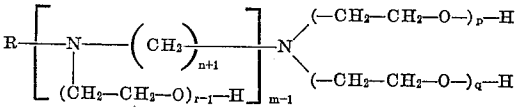


in which R represents an aliphatic hydrocarbon radical containing from 12 to 22 carbon atoms, *m*, *n*, *p*, *q* and *r* each represent a whole number, *m* and *n* being at the most 2 and the sum $p+q+(m-1)(r-1)$ being at least 3 and at the most 20.

6. A process for dyeing wool, which comprises treating the wool fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound represented by the formula

$$Me(F_2-SO_3H)_2$$

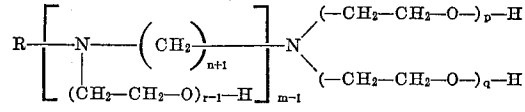
in which Me represents a complex-forming metal selected from the group consisting of chromium and cobalt and F_1-SO_3H represents a monoazo dyestuff capable of forming complex metal compounds, and carrying out the treatment in the presence of a compound which corresponds to the formula



in which R represents an aliphatic hydrocarbon radical containing from 12 to 22 carbon atoms, *m*, *n*, *p*, *q* and *r* each represent a whole number, *m* and *n* being at the most 2 and the sum $p+q+(m-1)(r-1)$ being at least 3 and at the most 20.

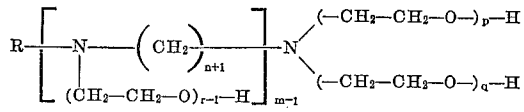
7. A process for dyeing wool, which comprises treating the wool fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound

of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two acid groups imparting solubility in water, carrying out the treatment at a pH-value below 6 in the presence of a compound which corresponds to the formula



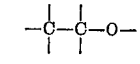
in which R represents an aliphatic hydrocarbon radical containing from 12 to 20 carbon atoms, *m*, *n*, *p*, *q* and *r* each represent a whole number, *m* and *n* being at the most 2 and the sub $p+q+(m-1)(r-1)$ being at least 3 and at the most 20, and, when the fibers have absorbed the desired quantity of dyestuff, raising above 6 the pH-value of the dyebath.

8. A process for dyeing a mixture of wool and cellulosic fibers which comprises treating the mixed fibers in an aqueous medium with a dyestuff consisting essentially of a 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two acid groups imparting solubility in water, carrying out this treatment at a pH-value below 6 in the presence of a compound which corresponds to the formula



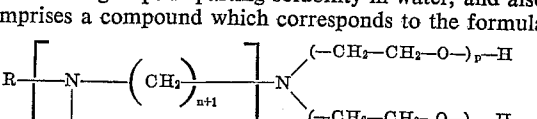
in which R represents an aliphatic hydrocarbon radical containing from 12 to 20 carbon atoms, *m*, *n*, *p*, *q* and *r* each represent a whole number, *m* and *n* being at the most 2 and the sum $p+q+(m-1)(r-1)$ being at least 3 and at the most 20, and, when the wool fibers have absorbed the desired quantity of dyestuff, raising above 6 the pH-value of the dyebath and then dyeing the cellulose fibers in the same bath with a substantive dyestuff.

9. A dyestuff preparation which comprises a dyestuff consisting essentially of 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two groups imparting solubility in water, and also comprises a compound which contains at least one basic nitrogen atom to which is bound at least one radical containing a polyglycol ether chain, the molecule containing at least 3



groups and at least 4 carbon atoms not belonging to such group.

10. A dyestuff preparation which comprises a dyestuff consisting essentially of 1:2-metal complex compound of an azo-dyestuff which compound is selected from the group consisting of chromium and cobalt compounds and contains in the molecule of the metal complex at least two groups imparting solubility in water, and also comprises a compound which corresponds to the formula



in which R represents an aliphatic hydrocarbon radical containing from 12 to 22 carbon atoms, *m*, *n*, *p*, *q* and *r* each represent a whole number, *m* and *n* being at the most 2 and the sum $p+q+(m-1)(r-1)$ being at least 3 and at the most 20.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

2,763,530	Schuetz et al.	Sept. 18, 1956
2,835,550	Laucius et al.	May 20, 1958
2,857,235	Coscia	Oct. 21, 1958
2,900,218	Gray	Aug. 18, 1959
2,914,531	Staeuble et al.	Nov. 24, 1959

2,933,489	Biedermann et al.	Apr. 19, 1960
2,967,755	Keller	Jan. 10, 1961
2,983,651	Seemuller	May 9, 1961

OTHER REFERENCES

Widmar et al.: 31,606, vol. 644, p. 914, March 20, 1951.