

UNITED STATES PATENT OFFICE

2,352,701

PROCESS OF PRODUCING FAST DYEINGS AND THE DYED FIBER OBTAINED THEREBY

Erich Fischer, Bad Soden in Taunus, Werner
Kirst, Königstein in Taunus, and Walter
Gmelin, Bad Soden in Taunus, Germany, as-
signors to General Aniline & Film Corporation,
New York, N. Y., a corporation of Delaware

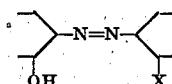
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11 Claims. (Cl. 8-22)

The present invention relates to a process of producing fast dyeings on animal fibers and cellulose fibers as well as on mixtures of animal fibers with cellulose fibers, furthermore on structures from synthetic polyamides of high molecular weight, and to the dyed fiber obtained thereby.

We have found that valuable dyeings of good properties of fastness can be obtained on animal fibers and natural or artificial cellulose fibers as well as on mixtures of animal fibers with cellulose fibers, furthermore on structures from synthetic polyamides of high molecular weight, by subjecting to a treatment with an agent yielding metal a dyestuff which does not contain a grouping capable of forming a metal complex compound and has been obtained by applying to the fiber a water-soluble or water-insoluble compound of the aromatic or heterocyclic series containing in the molecule an amino-group capable of being diazotized, then diazotizing and developing the dyestuff by means of an alkaline treatment.

It is surprising that the fastness to wet-processing of the dyeings, particularly their fastness to water, to perspiration, to washing, to fulling and to potting is essentially improved by the after-treatment with an agent yielding metal, since the dyestuffs produced on the fiber do not contain the known configurations capable of forming a metal complex compound, such as, for instance, the salicylic acid grouping or the



wherein X stands for OH, COOH, NH₂ or OCH₃. The said improvement in the properties of fastness is obtained on animal fibers as well as on cellulose fibers, and in general the shade is not so much displaced as is usually observed when metal complex compounds are formed.

The treatment with the agents yielding metal may be performed in the presence of organic dispersing agents, whereby the fastness to rubbing of the dyeings is in many cases improved.

The dyestuffs used as parent materials in the present process are those described, for instance, in U. S. Patents 2,205,481, 2,208,932, 2,213,193, 2,248,091, 2,263,559, 2,228,317, and 2,243,213, and in U. S. application Ser. No. 248,179, filed December 29, 1938, in the name of Konrad Renn, for "Process of producing fast dyeings and the dyed fiber obtained thereby," U. S. patent application

Serial No. 221,715, filed July 28, 1938, in the name of Werner Kirst, for "Process of producing fast dyeings and the dyed fiber obtained thereby," U. S. patent application Serial No. 261,378, filed March 11, 1939, in the name of Georg Kraenzlein, Werner Kirst, Carl Josef Mueller, and Willy Schumacher, for "Process of producing fast dyeings and the dyed fiber obtained thereby."

As agents yielding metal there may, for instance, be used chromium salts, such as chromium fluoride, chromium sulfate, chromium acetate, potassium bichromate; copper salts, such as copper sulfate; cobalt salts, such as cobalt nitrate, cobalt sulfate, cobaltous chloride; nickel salts, such as nickel sulfate; aluminium salts, such as aluminium acetate; iron salts, such as ferric sulfate; manganese salts, such as manganous chloride, manganese nitrate, manganese sulfate; furthermore, cadmium sulfate, uranium nitrate, vanadium chloride, strontium chloride and the like.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

1. 1 kilo of mixed yarn consisting of 50 parts of wool and 50 parts of staple fiber from viscose is treated for 1 hour at 95° C. in 24 liters of water containing 50 grams of the dyestuff 1-amino-5-hydroxynaphthalene-7-sulfonic acid-Cleve's acid-2-amino-8-hydroxynaphthalene-6-sulfonic acid and 80 grams of ammonium sulfate. 600 grams of sodium sulfate, dissolved in 6 liters of water, are then added and the material is further treated for half an hour at a temperature falling to 80° C. It is then rinsed, diazotized for half an hour in the cold in a bath containing per 30 liters of water 25 grams of sodium nitrite, 12 grams of sodium dibutyl-naphthalene-sulfonate and 75 cc. of hydrochloric acid of 20° Bé., and developed for half an hour in a solution containing per 30 liters of cold water 75 cc. of ammonia of 25 percent. strength and 10 grams of the condensation product from 1 mol of octodecylalcohol and 20 mols of ethylene oxide. The material is then rinsed and treated for ¾ to 1 hour at 95° C. in a bath containing per 30 liters of water 20 grams of potassium bichromate, 20 cc. of formic acid of 85 per cent. strength and 5 grams of the condensation product from 1 mol of octodecylalcohol and 20 mols of ethylene oxide.

The black dyeing thus obtained has practically the same shade as the dyeing produced without after-treatment with a metal salt. The fastness to water, to perspiration, to washing, to potting and to fulling is essentially improved.

The dyeings developed by a treatment with chromium fluoride, chromium sulfate, chromium acetate, copper sulfate, cobalt nitrate, cobalt sulfate, aluminium acetate, manganous chloride, nickel sulfate, vanadium chloride, uranium nitrate, strontium chloride and acetic acid likewise show a considerable improvement in their fastness to wet-processing.

2. 1 kilo of mixed yarn consisting of 50 parts of wool and 50 parts of staple fiber from viscose is treated for $\frac{3}{4}$ hour at 90° C. in 30 liters of water containing 40 grams of the dyestuff 1-amino-5-hydroxynaphthalene-7-sulfonic acid $\rightarrow$ Cleve's acid, 40 grams of ammonium sulfate and 600 grams of sodium sulfate, and the material is further treated for $\frac{3}{4}$ hour at a temperature falling to 75° C. It is then rinsed, diazotized as described in Example 1, and the dyestuff is developed to a dark-brown dyeing in an ammoniacal bath and rinsed again. The dyeing thus obtained is treated for 1 hour at 90° C. in a solution containing per 30 liters of water 20 grams of chromium fluoride and 20 cc. of acetic acid of 50 per cent. strength, rinsed and dried.

The brown dyeing thus obtained is essentially faster to water, to perspiration and to washing than the dyeing produced without treatment with an agent yielding metal.

3. 1 kilo of mixed yarn consisting of 50 parts of wool and 50 parts of staple fiber from cuprammonium cellulose is treated for 1 hour at 75° C. in 24 liters of water containing 40 grams of the dyestuff obtainable by coupling diazotized 1-amino-3-chloro-4-nitrobenzene with 2-amino-5-hydroxynaphthalene-7-sulfonic acid, in an acid medium, and subsequently reducing the nitro-group, and 50 grams of ammonium sulfate. 600 grams of sodium sulfate, dissolved in 6 liters of cold water, are then added and the material is further treated for half an hour at 60° C. It is then rinsed, diazotized and developed by means of ammonia, as described in Example 1, rinsed again and after-treated for one hour at 90° C. in a bath containing per 30 liters of water 20 grams of potassium bichromate and 20 cc. of acetic acid of 50 per cent. strength. The fastness to water, to perspiration, to washing and to potting of the dyeing after-treated with the chromium salt is essentially better than that of the dyeing which has not been after-treated.

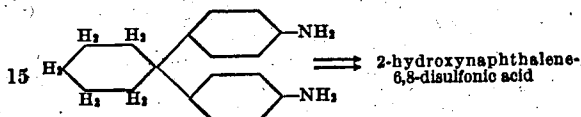
4. 1 kilo of a fabric consisting of 50 parts of

wool and 50 parts of staple fiber from viscose containing effects from acetate artificial silk is treated at 90° C. in a bath containing per 30 liters of water

40 grams of the dyestuff 4,4'-diaminodiphenyl-2,2'-disulfonic acid $\rightarrow$ 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid,

0.5 gram of the dyestuff diaminotriphenylmethane $\rightarrow$ 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone,

1 gram of the dyestuff:



10 grams of the condensation product from 1 mol of octodecylalcohol and 20 mols of ethylene oxide,

40 grams of ammonium sulfate and 600 grams of sodium sulfate.

The material is then allowed to stand for $\frac{3}{4}$ hour at a temperature falling to 70° C., rinsed and treated for half an hour in the cold in a bath containing

25 grams of sodium nitrite,
10 grams of sodium dibutyl-naphthalenesulfonate and
75 cc. of hydrochloric acid of 20° Bé.

in 30 liters of cold water, and developed for half an hour in a solution containing per 30 liters of cold water

75 cc. of ammonia of 25 per cent strength and 5 grams of the condensation product from 1 mol of octodecylalcohol and 20 mols of ethylene oxide.

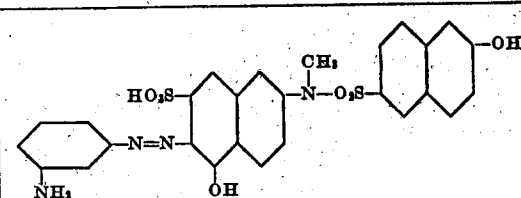
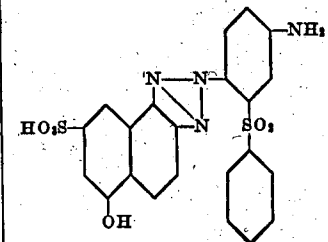
40 The material is then treated for 1 hour at 90° C. in a bath containing per 30 liters of water

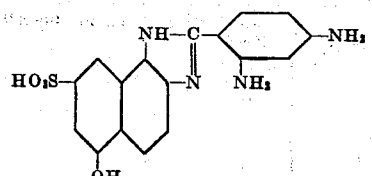
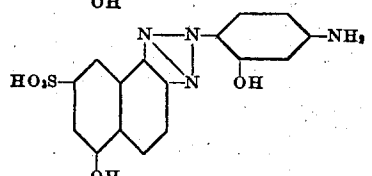
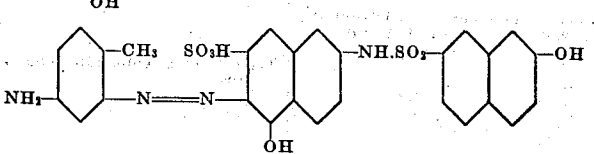
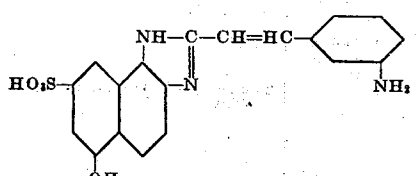
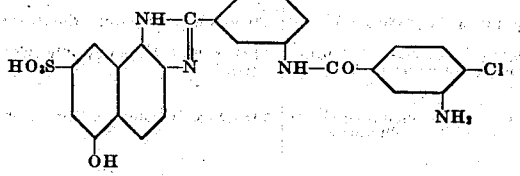
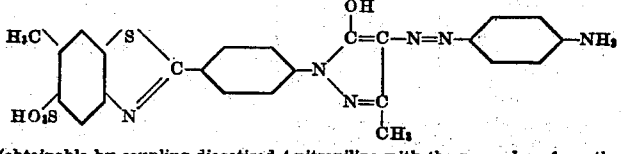
20 grams of chromium fluoride,
10 grams of glacial acetic acid and

45 5 grams of the condensation product of 1 mol of octodecylalcohol and 20 mols of ethylene oxide,

rinsed and dried. A yellow dyeing of very good properties of fastness is obtained. The effects from acetate artificial silk remain white.

The following table illustrates the shades of a number of other dyeings obtainable by the present invention:

	Parent component	Shade of the dyeing, treated with metal salts, on mixtures of wool and artificial silk staple fiber
1		Treated with copper sulfate: subdued red.
2		Treated with copper sulfate: yellow-brown.

	Parent component	Shade of the dyeing, treated with metal salts, on mixtures of wool and artificial silk staple fiber
3		Treated with potassium bichromate: red-brown.
4		Treated with copper sulfate: brown-orange.
5		Treated with potassium bichromate: red.
6	3'-aminobenzoyl-3'-aminobenzoyl-2-amino-5-hydroxynaphthalene-7-sulfonic acid → 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid.	Treated with potassium bichromate: subdued orange.
7		Treated with potassium bichromate: brown.
8	1-amino-5-hydroxynaphthalene-7-sulfonic acid → Cleve's acid → 2-amino-5-hydroxynaphthalene-7-sulfonic acid.	Treated with potassium bichromate: blue-black.
9	1-amino-5-hydroxynaphthalene-7-sulfonic acid → 1-amino-2,5-dimethylbenzene → Cleve's acid.	Treated with chromium fluoride: brown.
10	2-amino-5-hydroxynaphthalene-7-sulfonic acid → Cleve's acid → 2-amino-5-hydroxynaphthalene-7-sulfonic acid.	Treated with potassium bichromate: black.
11	2-amino-5-hydroxynaphthalene-7-sulfonic acid → Cleve's acid → 2-amino-8-hydroxynaphthalene-6-sulfonic acid.	Do.
12		Treated with potassium bichromate: yellowish-red.
13	1-amino-5-hydroxynaphthalene-3-sulfonic acid → 1-naphthylamine $\xrightarrow{\text{alkaline}}$ 1-amino-5-hydroxynaphthalene-7-sulfonic acid.	Treated with chromium fluoride: dark-blue.
14	2-amino-8-hydroxynaphthalene-6-sulfonic acid → 1-amino-3,5-dimethylbenzene → Cleve's acid.	Treated with copper sulfate: dark-brown.
15	1-amino-5-hydroxynaphthalene-7-sulfonic acid → Cleve's acid → Cleve's acid...	Treated with chromium fluoride: violet-brown.
16	4,4'-diaminodiphenylmonosulfonic acid $\begin{cases} \rightarrow 1-(4'-\text{aminophenyl})-3\text{-methyl-5-pyrazolone} \\ \rightarrow 1,3\text{-diaminobenzene} \\ \rightarrow 3\text{-aminoacetanilide} \end{cases}$	Treated with potassium bichromate: copper-brown.
17	4,4'-diaminodiphenylmonosulfonic acid $\rightarrow$ resorcinol	Treated with copper sulfate: brown.
18	1-amino-5-hydroxynaphthalene-7-sulfonic acid → 3'-aminobenzoyl-2-amino-5-hydroxynaphthalene-7-sulfonic acid.	Treated with potassium bichromate: dull violet.
19	1-(4'-aminobenzoylamino)-7-hydroxynaphthalene-3-sulfonic acid → 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid.	Treated with copper sulfate: brown-orange.
20	3'-aminobenzoyl-3'-aminobenzoyl-2-amino-5-hydroxynaphthalene-7-sulfonic acid → 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid.	Do.
21	1-amino-7-hydroxynaphthalene-3-sulfonic acid → 1-aminonaphthalene → 1-amino-8-hydroxynaphthalene-4-sulfonic acid.	Treated with chromium fluoride: blue-black.
22	 (obtainable by coupling diazotized 4-nitraniline with the pyrazolone from the hydrazine of the dehydrothiotoluidine sulfonic acid, and reducing the nitro-group).	Treated with chromium fluoride: subdued orange.

	Parent component	Shade of the dyeing, treated with metal salts, on mixtures of wool and artificial silk staple fiber
23	(obtainable by coupling 2 mols of diazotized 3-nitraniline with the bispyrazolone from the hydrazine of 4,4'-diamino-stilbene-2,2'-disulfonic acid, and reducing the nitro-groups).	Treated with chromium fluoride: golden yellow.
24	(obtainable by coupling diazotized dehydrothioluminesulfonic acid with 1-(3'-amino-phenyl)-5-pyrazolone-3-carboxylic acid).	Treated with chromium fluoride: golden orange.
25	(obtainable by coupling diazotized 4'-nitrobenzoyl-1,4-diaminobenzene-2-sulfonic acid with 1-(3'-aminophenyl)-3-methyl-5-pyrazolone and reducing the nitro-group).	Treated with chromium fluoride: golden yellow.
26	1-(3'-aminobenzoylamino)-3-aminobenzene $\longrightarrow$ 2-mols of 1-(3'-nitrophenyl)-5-pyrazolone-3-carboxylic acid and reduction of the nitro-groups).	Treated with chromium fluoride: yellow.
27	1-(4'-nitrobenzoylamino)-4-aminobenzene $\longrightarrow$ 1-phenyl-5-pyrazolone-3-carboxylic acid, reduced $\longrightarrow$ 4'-aminobenzoyl-2-amino-5-hydroxynaphthalene-7-sulfonic acid.	Treated with chromium fluoride: yellowish-red.
28	2,4-diaminotoluene-5-sulfonic acid $\longrightarrow$ metaphenylenediamine.	Treated with copper sulfate: brown.
29	(Schultz, "Farbstofftabellen," 7th edition, volume 1, No. 621.)	Treated with chromium fluoride or copper sulfate: black.
30	(obtainable by condensing 4,4'-diaminodiphenylurea-3,3'-disulfonic acid with 2 mols of 4-nitrobenzoylchloride, reducing and coupling the tetrazotized compound with 2 mols of 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid; cf. German patent specification 629,812).	Treated with chromium fluoride: golden yellow.

	Parent component	Shade of the dyeing, treated with metal salts, on mixtures of wool and artificial silk staple fiber
31		Treated with potassium bichromate: brown.
32		Treated with chromium fluoride: red.
33		Do.
34	1-amino-5-hydroxynaphthalene-7-sulfonic acid $\longrightarrow$ Cleve's acid $\longrightarrow$ 2-amino-8-hydroxynaphthalene-6-sulfonic acid.	Shade of the dyeing, treated with metal salts, on polyamide silk Treated with potassium bichromate: black.
35	1-amino-6-naphthol	Shade of the dyeing, treated with metal salts, on acetate silk Treated with chromium fluoride or potassium bichromate: reddish black.
36		Treated with chromium fluoride or potassium bichromate: reddish brown.
37		Treated with chromium fluoride: golden orange.
38	(obtainable by coupling diazotized 1-(4'-nitrobenzoylamino)-4-aminobenzene-3-sulfonic acid with 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone, reducing the nitro-group to the amino-group, and further diazotizing the aminomonazo-dyestuff thus obtained and coupling it with 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid).	Treated with chromium fluoride: golden yellow.
39	4,4'-diaminodiphenyl-2,2'-disulfonic acid $\rightleftharpoons$ 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid.	Do.
40	4,4'-diaminodiphenyl-3,3'-disulfonic acid $\rightleftharpoons$ 4-acetoacetyl-amino-1-aminobenzene	Treated with chromium fluoride: yellow.

	Parent component	Shade of the dyeing, treated with metal salts, on mixtures of wool and artificial silk staple fiber
41	(obtainable by coupling diazotized 1-(4'-nitrobenzoylamino)-4-aminobenzene-3-sulfonic acid with 1-(3'-aminophenyl)-5-pyrazolone-3-carboxylic acid, transforming the amino-group into the aceto-acetylamino-group and reducing the nitro-group to the amino-group).	Treated with chromium fluoride: yellow.
42	(obtainable by coupling diazotized 1-(4'-nitrobenzoylamino)-4-aminobenzene-3-sulfonic acid with 4-amino-4'-acetamidoaminodiphenyl-3-sulfonic acid and reducing the nitro-group to the amino-group).	Treated with chromium fluoride: yellow.
43	(obtainable by coupling 2 mols of diazotized 4-nitro-1-aminobenzene with 1 mol of 4,4'-bis-acetoacetyl-aminostilbene-2,2'-disulfonic acid and reducing the nitro-groups to the amino-groups).	Do.

We claim:

1. A process of producing fast dyeings which comprises applying to the fiber a compound of the group consisting of the aromatic and heterocyclic series which contains in the molecule an amino group capable of being diazotized, and in addition thereto a member of the group consisting of amino and hydroxyl groups, but is free from a grouping capable of forming a metal complex compound, then diazotizing on the fiber and subjecting the dyeing to an alkaline treatment and subsequently to a treatment with an agent yielding a metal.

2. A process of producing fast black dyeings which comprises applying to the fiber the water-soluble azo dyestuff 1-amino-5-hydroxynaphthalene-7-sulfonic acid→Cleve's acid→2-amino-8-hydroxynaphthalene-6-sulfonic acid, then diazotizing on the fiber and subjecting the dyeing to an alkaline treatment and subsequently to a treatment with an agent yielding a metal.

3. A process of producing fast black dyeings which comprises applying to mixtures of wool and artificial silk staple fiber the water-soluble azo dyestuff 1-amino-5-hydroxynaphthalene-7-sulfonic acid→Cleve's acid→2-amino-8-hydroxynaphthalene-6-sulfonic acid, then diazotizing on the fiber and subjecting the dyeing to an alkaline treatment and subsequently to a treatment with an agent yielding chromium.

4. A process of producing fast blue-black dyeings which comprises applying to the fiber the water-soluble azo dyestuff 1-amino-5-hydroxynaphthalene-7-sulfonic acid→Cleve's acid→2-amino-5-hydroxynaphthalene-7-sulfonic acid, then diazotizing on the fiber and subjecting the dyeing to an alkaline treatment and subsequent-

ly to a treatment with an agent yielding a metal.

5. A process of producing fast blue-black dyeings which comprises applying to mixtures of wool and artificial silk staple fiber the water-soluble azo dyestuff 1-amino-5-hydroxynaphthalene-7-sulfonic acid→Cleve's acid→2-amino-5-hydroxynaphthalene-7-sulfonic acid, then diazotizing on the fiber and subjecting the dyeing to an alkaline treatment and subsequently to a treatment with an agent yielding chromium.

6. A process of producing fast brown dyeings which comprises applying to the fiber the water-soluble azo dyestuff 1-amino-5-hydroxynaphthalene-7-sulfonic acid→Cleve's acid→Cleve's acid, then diazotizing on the fiber and subjecting the dyeing to an alkaline treatment and subsequently to a treatment with an agent yielding a metal.

7. A process of producing fast brown dyeings which comprises applying to mixtures of wool and artificial silk staple fiber the water-soluble azo dyestuffs 1-amino-5-hydroxynaphthalene-7-sulfonic acid→Cleve's acid→Cleve's acid, then diazotizing on the fiber and subjecting the dyeing to an alkaline treatment and subsequently to a treatment with an agent yielding chromium.

8. Fiber dyed with a dyestuff by the process claimed in claim 1.

9. Fiber dyed with a dyestuff by the process claimed in claim 2.

10. Fiber dyed with a dyestuff by the process claimed in claim 4.

11. Fiber dyed with a dyestuff by the process claimed in claim 6.

ERICH FISCHER.
WERNER KIRST.
WALTER GMEIN.