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NEW DYEING PREPARATION AND ITS CONVERSION TO DYESTUFFS

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20 Claims. (Cl. 8—6)

Our present invention relates to new dyeing preparations and their conversion to dyestuffs.

These dyeing preparations contain a diazo-sulfonate of the diarylamine series corresponding to the probable general formula:

X—NH—R—N=N—SO_3—alkali-metal,

wherein X means a naphthalene nucleus or a radical of the benzene series which may contain in the para-position to the NH-group a further —N=N—SO_3—alkali-metal group and R means a radical of the benzene series and a combining component containing a hydroxy or a O-alkali-metal group whereof the adjacent position is capable of attaching an arylazogroup.

As substituents present in the benzene nuclei of the diazo-sulfonates may be specifically named: alkyl, alkoxy, aryloxy, alkylmercapto, aroylamino, halogen, nitro, arylsulfonyl, arylaminocarbonyl.

The diazo-sulfonates we use in our present invention are described and claimed in the copending U. S. application Serial No. 561,087 filed on September 3, 1931, in the name of Arthur Zitscher and Wilhelm Seidenfaden.

As combining components of the aforesaid kind may be named: 2-hydroxynaphthalene, its nuclear substitution products, as, for instance, aroylamino-hydroxynaphthalenes, (2-hydroxy-naphthalene-3-carbonyl)-amino-aryls (as described in U. S. Patents Nos. 1,101,111 and 1,140,747), (6-halogen- or arylamino-2-hydroxy-naphthalene-3-carbonyl)-amino-aryls (see German Patent No. 396,519 and British Patent No. 330,349); derivatives of 1-hydroxy-naphthalene-4-carboxylic acid (see U. S. Patent No. 1,453,660), as, for instance, 1-hydroxy-naphthalene-4-phenyl-ketone; compounds containing an acidic methylene group capable of being combined with diazocompounds, as, for instance pyrazolones and derivatives of β-ketonaldehyde, for instance, acetoacetyl-amino-aryls and di-(aceto-acetyl-amino)-aryls (see U. S. Patent Nos. 1,594,864, 1,594,866, 1,594,867, 1,580,709, 1,634,090); dihydroxy-quinolines (see U. S. applications Serial Nos. 352,317, 352,318, 352,319; British Patent No. 332,940); (2-hydroxy-carbazole-3-carbonyl)-amino-aryls, (2-hydroxy-benzocarbazole-3-carbonyl)-amino-aryls, (2-hydroxy-anthracene-3-carbonyl)-amino-aryls.

These dyeing preparations yield, when applied in an alkaline medium to fibers, by steaming only, insoluble azodyestuffs on the fibers.

Such applying to the fibers consists in dyeing according to the one-bath-method or in printing. The dyebath or the printing paste or also the powderous dyeing preparations themselves are advantageously mixed with dyeing expedients having wetting, emulsifying or dissolving properties, or also with the additional agents customary in using nitrosamine-printing-colors, as, for instance chromate. Furthermore sulfur is advantageously added to the printing paste. Thereby the quickness and the evenness of the dyestuff formation is favorably influenced.

In order to further illustrate our invention the following examples are given, the parts being by weight and all temperatures in centigrade degrees. But we wish it to be understood that we are not limited to the particular conditions or specific products mentioned therein.

Example 1

A printing paste which contains:
63 parts of the sodium salt of diphenylamine-4.4'-bisdiazo-sulfonic acid
25 parts of (2-hydroxy-naphthalene-3-carbonyl-amino) benzene
30 parts of caustic soda lye of 34° Bé.
20 parts of thiodiglycol
362 parts of water
500 parts of starch tragacanth-thickening
is printed on textile materials. The goods thus printed are dried, steamed for 7 minutes in the Mather-Platt, rinsed hot and shortly soaped.

In this manner a beautiful bluish black print is obtained.

Example 2

By using a printing paste which contains 20 parts 1-(2-hydroxy-carbazole-3-carbonyl-amino)-2-methyl-benzene, 50 parts of diphenylamine-4.4'-bis-diazosulfonate and the other ingredients of the paste used in Example 1 and by working otherwise as described above, a puce-brown print is obtained.

4.4'-di-(aceto-acetylamino)-3.3'-dimethyl-diphenyl yields by an analogous process a brown orange print.

Example 3

A printing paste which contains:
20 parts of the sodium salt of 4'-methoxy-diphenyl-amine-4-diazo-sulfonic-acid
15 parts of (2-hydroxy-naphthalene-3-carbonyl-amino)-benzene
20 parts of caustic soda lye of 34° Bé.
15 parts of thiodiglycol
430 parts of water
500 parts of starch tragacanth-thickening
is printed on the materials. Then the goods are

dried, steamed for 7 minutes in the Mather-Platt, rinsed hot, soaped and rinsed again.

In this manner a clear navy-blue print is obtained.

Diphenyl-amine-4-diazo-sulfonate yields when used in an analogous manner a more reddish navy-blue print.

Example 4

A printing paste which contains
22 parts of the sodium salt of diphenyl-amine-4.4'-bis-diazo-sulfonic acid
25 parts of 1-(2-hydroxy-naphthalene-3-carbonyl-amine)-2-methoxy-benzene
30 parts of caustic soda lye of 34° Bé.
8 parts of finely powdered sulfur
20 parts of thiodiglycol
395 parts of water
500 parts of starch-tragacanth-thickening
is printed, the goods are steamed for 5 minutes, rinsed hot and soaped. In this manner a full black print is obtained.

Example 5

A printing paste which contains:
20 parts of the sodium salt of 4'-methoxy-diphenyl-amine-4-diazo-sulfonic-acid
15 parts of (2-hydroxy-naphthalene-3-carbonyl-amino)-benzene
20 parts of caustic soda lye of 34° Bé.
4 parts of finely powdered sulfur
20 parts of alcohol
15 parts of Turkey-red-oil
15 parts of sodium chromate solution 1:4
391 parts of water
500 parts of starch-tragacanth-thickening
is printed. The goods are dried, steamed for 5 minutes in the Mather-Platt and finished as described above.

In this manner a dark navy-blue print is obtained; by using a paste of lower concentration beautiful light blue shades are obtained.

Example 6

A bleached calico fabric is impregnated in a solution which contains:
20 parts of the sodium salt of 4'-methoxy-diphenyl-amine-4-diazo-sulfonic-acid
15 parts of (2-hydroxy-napthalene-3-carbonyl-amino)-benzene
20 parts of caustic potash-lye of 34° Bé.
15 parts of alcohol
15 parts of thiodiglycol
15 parts of sodium-chromate solution 1:4
50 parts of mucilage of tragacanth 65:1000
50 parts of water
The fabric is dried and steamed for 7–10 minutes in the Mather-Platt. Then it is rinsed hot and soaped at the boil.

In this manner a blue-self-colored dyeing is obtained.

Example 7

A printing paste which contains:
16 parts of the sodium salt of 3-methoxy-diphenyl-amine-4-diazo-sulfonic-acid
15 parts of 1-(2-hydroxy-naphthalene-3-carbonyl-amino)-3-nitro-benzene
30 parts of alcohol
6 parts of caustic soda lye of 34° Bé.
5 parts of thiodiglykol
454 parts of water
450 parts of starch-tragacanth-thickening
15 parts of neutral chromate solution 1:4
is printed. The goods are dried, steamed for 7 minutes in the Mather-Platt and finished as described above.

In this manner a greenish blue print is obtained.

Example 8

A mixture of:
32.0 parts of the sodium salt of 4'-methoxy-diphenyl-amine-4-diazo-sulfonic-acid
26.3 parts of (2-hydroxy-naphthalene-3-carbonyl-amino)-benzene
6.0 parts of finely ground sulfur
8.0 parts powdered sodium hydroxide
is ground together. The mixture is made up to a printing paste. This paste is printed on the materials, which are then steamed and washed.

In this manner a clear navy blue print is obtained.

Example 9

A mixture of:
10.6 parts of the sodium salt of 3-methoxy-diphenyl-amine-4-diazo-sulfonic-acid
10.0 parts of 1-(-2-hydroxy-naphthalene-3-carbonyl-amino)-3-nitro-benzene
3.0 parts of sodium hydroxide
is ground together. The mixture is made up to a printing paste. This paste is printed on the materials, which are then steamed and washed.

In this manner a greenish blue print is obtained.

Example 10

A mixture of:
30.0 parts of the disodium salt of diphenylamine-4.4'-bis-diazo-sulfonic acid
28.6 parts of the di-sodium salt of 1-(2-hydroxy-naphthalene-3-carbonyl-amino)-3-nitro-benzene
8.0 parts of flowers of sulfur
is ground together. The mixture is made up to a printing paste, advantageously with the addition of caustic soda lye. This paste is printed on the materials, which are then steamed and washed. In this manner a black print is obtained.

In the following table we have inserted the shades of a series of further dyeings or prints, produced in an analogous manner:

Salt of the diazosulfonic acid of	(2-hydroxy-naphthalene-3-carbonyl) compound of	Shade
4-amino-diphenylamine	2-amino-1-ethoxy-benzene	Dark-blue
Do	5-chloro-2-amino-1-methoxy-benzene	Navy-blue
Do	2-amino-1-phenoxy-benzene	Blue
4-amino-2'-methyl-diphenylamine	1-amino-2.5-dimethoxy-benzene	Reddish navy-blue
4-amino-2'-methoxy-diphenylamine	2-amino-1-ethyl-benzene	Dark-violet
Do	2-amino-3-methoxy-naphthalene	Blackish blue
4-amino-2'-ethoxy-diphenylamine	2-amino-naphthalene	Dark-blue
Do	2-amino-4-chloro-1-ethyl-benzene	Dark-blue
4-amino-2'-phenoxy-diphenylamine	2-ethoxy-1-amino-benzene	Reddish navy-blue
4-amino-2'-chloro-diphenylamine	3-nitro-1-amino-benzene	Dark-blue
Do	1-amino-4-ethyl-benzene	Reddish navy-blue
4-amino-3'-methyl-diphenylamine	5-chloro-2-amino-1-methoxy-benzene	Reddish navy-blue
4-amino-3'-methoxy-diphenylamine	2-amino-1-methyl-benzene	Reddish dark-blue
4-amino-3'-chloro-diphenylamine	3-amino-1-methyl-benzene	Navy-blue
4-amino-4'-methyl-diphenylamine	4-amino-1-methyl-benzene	Reddish dark-blue

Salt of the diazosulfonic acid of	(2-hydroxy-naphthalene-3-carbonyl) compound of	Shade
4-amino-4'-methyl-diphenylamine	5 - chloro - 2 - amino - 1 - methyl-benzene	Reddish navy-blue
4 - amino - 4' - methoxy - diphenylamine	2-amino-1-methoxy-benzene	Dark-blue
Do	4 - amino - 1 - methoxy - benzene	Do.
Do	3 - chloro - 1 - amino - benzene	Do.
Do	5 - chloro - 2 - amino - 1 - methyl-benezne	Blue
Do	4 - chloro - 2 - methoxy - 1 - amino-benzene	Dark-blue
Do	2-amino-naphthalene	Reddish navy-blue
Do	(4' - amino - benzoylamino)-benzene	Blue
Do	1 (4' - amino - benzoylamino) - 2 - methoxy - benzene	Do.
Do	3-amino-1-acetyl-benzene	Greenish blue
Do	3 - amino - 4 - methoxy - 1 - (dimethyl - aminosulfoyl)-benzene	Blue
Do	2 - amino - 4 - ethylsulfonyl - 1- methyl - benzene	Greenish blue
4 - amino - 4' - ethoxy - diphenylamine	amino-benzene	Do.
Do	2-amino-1-methyl-benzene	Dark-blue
Do	3-amino-1-methyl-benzene	Do.
Do	4 - amino - 1 - methoxy - benzene	Do.
Do	3-amino-1-chloro-benzene	Greenish blue
Do	3.4 - dichloro - 1 - amino - benzene	Blue
Do	2-amino-naphthalene	Reddish navy-blue
4-amino-4'-ethoxy-diphenylamine	1 (4'-amino-benzoylamino)-2-methyl-benzene.	Blue
Do	1 (4'-amino-benzoylamino)-3-nitro-benzene.	Do.
4-amino-4'-phenoxy-diphenylamine	4-amino-1 ethoxy-benzene	Reddish dark-blue
4-amino-4'-methylmercapto-diphenylamine	4-chloro-1-amino-benzene	Blue
4-amino-4'-chloro-diphenylamine	2-methoxy-1-amino benzene	Reddish navy blue
4-amino-4'-benzoylamino-diphenylamine	2-chloro-1-amino-benzene	Clear-blue
4-amino-2-methyl-4'-methoxy-diphenylamine	2-ethoxy-1-amino-benzene	Reddish blue
Do	3-chloro-1-amino-benzene	Greenish blue
Do	1-amino-naphthalene	Blue
4-amino-3-methyl-4'-methoxy-diphenylamine	amino-benzene	Blue
Do	1-amino-napthalene	Indigo-blue
Do	2-methyl-1-amino-benzene	Dark-blue
4-amino-3'-methyl-6'-methoxy-diphenylamine	3-methyl-1-amino-benzene	Do.
4-amino-3-methyl-4'-chloro-diphenylamine	amino-benzene	Reddish dark-blue
4-amino-2'-methyl-4'-chloro-diphenylamine	3-nitro-1-amino-benzene	Deep-violet
4-amino-2'-methyl-5'-chloro-diphenylamine	1-amino-naphthalene	Reddish navy-blue
4-amino-3'-methyl-6'-chloro-diphenylamine	4-chloro-2-methoxy-1-amino-benzene	Dark-violet
4 - amino - 4' - methyl - 3-chloro-diphenylamine	2-methyl-1-amino-benzene	Blue-violet
Do	3-nitro-1-amino-benzene	Greenish blue
4 - amino - 4' - methyl - 3'-chloro-diphenylamine	amino-benzene	Reddish navy-blue
4 - amino - 2' - methoxy - 4'-chloro-diphenylamine	1 - amino - 2.5 - dimethoxy-benzene	Deep-violet
4 - amino - 3.2' - dimethyl-diphenylamine	amino-benzene	Reddish dark-blue
Do	2 - methoxy - 1 - amino-benzene	Do.
4 - amino - 3.4' - dimethyl-diphenylamine	4 - chloro - 2 - methyl - 1-amino-benzene	Dark-blue
4 - amino - 3.2' - dimethoxy-diphenylamine	4 - chloro - 2 - methyl - 1-amino-benzene	Reddish blue
4 - amino - 3.4' - dimethoxy-diphenylamine	5 - chloro - 2 - methoxy - 1-amino-benzene	Reddish blue
Do	2-amino-naphthalene	Greenish blue
Do	4 - chloro - 2 - methyl - 1-amino-benzene	Do.
4 - amino - 2.4' - dimethoxy-diphenylamine	amino-benzene	Dark-blue
4-amino - 3'.4' - dimethoxy-diphenylamine	4-chloro-1-amino-benzene	Do
4 - amino - 3.2' - dichloro-diphenylamine	amino-benzene	Dark-violet
4 - amino - 3.4' - dichloro-diphenylamine	4-chloro - 2.5 - dimethoxy-1-amino-benzene	Reddish violet
4 - amino - 3' .4' - dichloro-diphenylamine	3 - methoxy - 1 - amino-benzene	Blackish violet
4-amino-3-methoxy-6.2'-dimethyl-4'-chloro-diphenylamine	4-chloro-1-amino-benzene	Violet
4-amino-3-methyl-5-chloro-4' - methoxy - diphenyl-amine	5 - chloro - 2 - methoxy - 1-amino-benzene	Reddish violet
4 - amino - 2' - nitro - diphenylamine	amino-benzene	Blackish garnet-blue
4 - amino - 3' - chloro- 6'-nitro-diphenylamine	2.5 - dimethoxy - 1 - amino-benzene	Brownish garnet
4 - amino- 2.5 - dimethyl - 3' - chloro - 6' - nitro - diphenylamine	2 - methyl - 1 - amino - benzene	Brownish garnet
4-amino - 2'.4' - dinitro - diphenylamine	1 - amino - 4 - methoxy - benzene	Do.
Do	1 - amino - 3 - methyl - 4 - methoxy - benzene	Do.
4 - amino - 3 - methyl - 2'.4' - dinitro - diphenyl-amine	1 - amino - 2 - methyl - 4 - methoxy-benzene	Bluish garnet
4 - amino - 3 - methoxy - 2'.4' - dinitro - diphenyl-amine	1-amino-3-nitro-benzene	Iron-garnet
4 - amino - 3 - chloro - 2'.4' - dinitro-diphenylamine	1 - amino - 2 - methyl - benzene	Brownish claret red
4 - amino - 3.2'.4' - trinitro-diphenylamine	1 - amino - 2.5 - dimethoxy-benzene	Bluish garnet
4 - amino - 2.5 - dimethoxy-2'.4' - dinitro - diphenyl-amine	amino benzene	Bluish black
Do	1 - amino - 2 - methyl - 4 - methoxy-benzene	Greenish black
Do	2 - amino - naphthalene	Do.
Do	1 - amino - 2 - ethoxy - benzene	Blackish green
Do	1 - amino - 3.4 - dimethoxy-5-chloro-benzene	Black
Do	1 - amino - 3 - methyl - 4 - methoxy-benzene	Black
4-amino-3'-(phenylamino-carbonyl)-diphenylamine	aminobenzene	Bluish violet
4 - amino - 3(4' - methyl - benzene-sulfonyl) - diphenylamine	1-amino-2-methyl-4-chloro-benzene	Blue
Do	1-amino-naphthalene	Navy blue
Do	1-amino-2-methyl-4-methoxy-benzene	Reddish blue
Do	1-amino-3-nitro-benzene	Blue
4-amino-3'-methyl-4'-methoxy-diphenylamine	1-amino-4-methoxybenzene	Reddish dark blue
Do	1-amino-3-methyl-4-methoxy-benzene	Navy blue
Do	1-amino-4-methylbenzene	Reddish dark blue
4-amino-3-methyl-diphenylamine	1-amino-3-nitro-benzene	Greenish blue
Do	1-amino-2-methyl-benzene	Dark blue
4-amino-3-methoxy-diphenylamine	amino-benzene	Reddish blue
Do	1-amino-3-methoxy-benzene	Blue
Do	1-amino-4-chloro-benzene	Blue
4-amino-4'-dimethyl-amino-diphenylamine	1-amino-2-methoxy-benzene	Greyish blue
4-amino-4'-nitro-diphenyl-amine	1-amino-2-methyl-benzene	Reddish black
2(4'-amino-phenylamino)-naphthalene	amino-benzene	Blue
Do	1-amino-4-methoxy-benzene	Reddish dark blue
Do	1-amino-3-chloro-benzene	Do.
4-amino-diphenyl-amine	4.4'-di-(2-hydroxynaphthalene - 3-carbonylamino)-3.3' - dimethoxy - diphenyl	Dark violet
4-amino-4'-methoxy-diphenylamine	(6-bromo - 2 - hydroxy-naphthalene-3-carbonyl-amino)-benzene	Dark blue
Do	1-(6 - bromo - 2 - hydroxy-naphthalene - 3 - carbonylamino) - 2 - methoxy-4-chloro-benzene	Dark navy blue.
Do	2-hydroxynaphthalene	Corinth
Do	1 - hydroxy - naphthalene-4-phenylketone	Corinth
Do	1-(2-hydroxy - anthracene-3- carbonylamino)- 2-methylbenzene	Bluish green
Do	1 - phenyl - 3 - methyl - 5-pyrazolone	Brownish red
Do	4.4' - di -(aceto - acetyl - amino) - 3.3' - dimethyl-diphenyl	Birght yellowish orange
Do	6.7 - benzo-2.4-dihydroxy-quinoline	Chocolate brown
4 - amino - 4' - ethoxy - diphenylamine	1 -(6 - bromo - 2 - hydroxy-naphthalene - 3- carbonylamino) - 2 - methoxy - benzene	Reddish dark blue

Salt of the diazosulfonic acid of	(2-hydroxy-naphthalene-3-carbonyl) compound of	Shade
4-amino-4'-ethoxy-diphenylamine	1-(6-bromo-2-hydroxy-naphthalene-3-carbonylamino)-naphthalene	Greenish blue
Do	1.4-di-(2-hydroxy-naphthalene-3-carbonylamino)-2-methyl-5-methoxy-benzene	Navy blue
Do	4.4'-di-(2-hydroxy-naphthalene-3-carbonylamino)-benzo-phenone	Greenish blue
4-amino-3-methoxy-diphenylamine	1-(2-hydroxy-anthracene-3 carbonyl-amino)-2-methyl-benzene	Bluish green
4.4'-diamino-diphenylamine	2-hydroxynaphthalene	Corinth
Do	1-(2-hydroxy-naphthalene-3-carbonylamino)-2-methyl-benzene	Black
Do	2-(2-hydroxy-naphthalene-3-carbonylamino)-naphthalene	Black
4.4'-diamino-2-chloro-3.3'-dimethyldiphenyl-amine	(2-hydroxy-naphthalene-3-carbonylamino)-benzene	Black

Since an object of the present invention is to produce dyestuffs of good fastness properties which dyestuffs are insoluble in water and alkalies, it is to be understood that the aromatic nuclei of the general formulæ appearing in the appended claims contain no substituents as are known to render organic compounds soluble in water or alkalies and to tend to depreciate the fastness of the dyestuffs to alkalies. Substituents of this kind are the sulfonic acid, the carboxylic acid and the hydroxy group.

We claim:

1. As new compositions of matter the dyeing preparations comprising a diazo-sulfonate of the diaryl-amine series corresponding to the probable general formula:

X—NH—R—N=N—SO_3—alkali-metal

wherein X means a naphthalene nucleus or a radical of the benzene series which may contain in the para-position to the NH-group a further —N=N—SO_3—alkali-metal group and R means a radical of the benzene series and a combining component containing a hydroxy or a O-alkali-metal group whereof the adjacent position is capable of attaching an arylazo group, which dyeing preparations yield in the presence of caustic alkali by steaming azo-dyestuffs insoluble in water and alkali.

2. As new compositions of matter the dyeing preparations comprising a diazo-sulfonate of the diarylamine series corresponding to the probable general formula:

X—NH—R—N=N—SO_3—alkali-metal

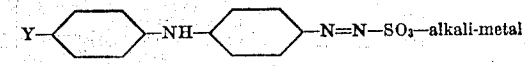
wherein X means a naphthalene nucleus or a radical of the benzene series which may contain in the para-position to the NH-group a further —N=N—SO_3—alkali-metal group and R means a radical of the benzene series and an azo coupling component which contains a hydroxy or a O-alkali-metal group, a free ortho-position relative to the said group capable of attaching an arylazo group and which may contain as substituents aroylamino, aroyl, arylaminocarbonyl, which dyeing preparations yield in the presence of caustic alkali by steaming azo dyestuffs insoluble in water and alkali.

3. As new compositions of matter the dyeing preparations comprising a diazo-sulfonate of the diphenylamine series corresponding to the probable general formula



wherein the benzene nuclei may contain alkyl, alkoxy, aryloxy, halogen or nitro and Y means hydrogen or one of the aforesaid substituents or a second—N=N—SO_3—alkali-metal group and a combining component containing a hydroxy or a O-alkali-metal group whereof the adjacent position is capable of attaching an arylazo group, which dyeing preparations yield in the presence of caustic alkali by steaming azo-dyestuffs insoluble in water and alkali.

4. As new compositions of matter the dyeing preparations comprising a diazo-sulfonate of the diphenylamine series corresponding to the probable general formula:

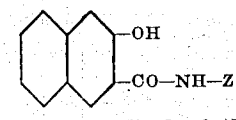


wherein the benzene nuclei may contain alkyl, alkoxy, aryloxy, halogen or nitro and Y means hydrogen or one of the aforesaid substituents or a second—N=N—SO_3—alkali-metal group and an azo coupling component which contains a hydroxy or a O-alkali-metal group, a free ortho-position relative to the said group capable of attaching an arylazo group and which may contain as substituents aroylamino, aroyl, arylaminocarbonyl, which dyeing preparations yield in the presence of caustic alkali by steaming azo-dyestuffs insoluble in water and alkali.

5. As new compositions of matter the dyeing preparations comprising a diazo-sulfonate of the diaryl-amine series corresponding to the probable general formula:

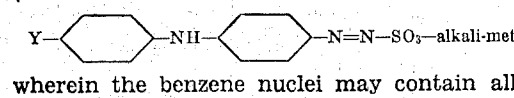
X—NH—R—N=N—SO_3—alkali-metal

wherein X means a naphthalene nucleus or a radical of the benzene series which may contain in the para-position to the NH-group a further —N=N—SO_3—alkali-metal group and R means a radical of the benzene series, and a (2-hydroxy-naphthalene-3-carbonyl)-amino-aryl of the formula:

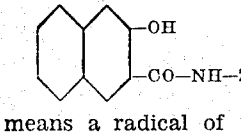


wherein Z means a radical of the benzene or naphthalene series, which dyeing preparations yield in the presence of caustic alkali by steaming azo-dyestuffs insoluble in water and alkali.

6. As new compositions of matter the dyeing preparations comprising a diazo-sulfonate of the diphenylamine series corresponding to the probable general formula:



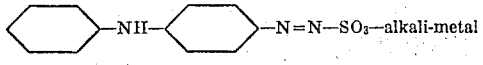
wherein the benzene nuclei may contain alkyl, alkoxy, aryloxy, halogen or nitro and Y means hydrogen or one of the aforesaid substituents or a second—N=N—SO_3—alkali-metal group, and a (2-hydroxy-naphthalene-3-carbonyl)-amino-aryl of the formula:



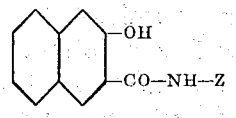
wherein Z means a radical of the benzene or naphthalene series, which dyeing preparations

yield in the presence of caustic alkali by steaming azo-dyestuffs insoluble in water and alkali.

7. As new compositions of matter the dyeing preparations comprising a diazo-sulfonate of the diphenylamine series corresponding to the probable general formula:



wherein the benzene nuclei may contain alkyl, alkoxy, aryloxy, halogen or nitro, and a (2-hydroxy-naphthalene-3-carbonyl)-amino-aryl of the formula:



(wherein Z means a radical of the benzene or naphthalene series), which dyeing preparations yield in the presence of caustic alkali by steaming azo-dyestuffs insoluble in water and alkali.

8. As a new composition of matter the dyeing preparation consisting of

32, 0 parts of the sodium salt of 4'-methoxy-diphenylamine-4-diazo-sulfonic acid
26, 3 parts of (2-hydroxy-naphthalene-3-carbonyl)-amino-benzene
6 parts of finely ground sulfur
8 parts of powderous sodium hydroxide,

which dyeing preparation yields, when brought onto fibers, by steaming clear navy blue dyeings and printings.

9. As a new composition of matter the dyeing preparation consisting of

10, 6 parts of the sodium salt of 3-methoxy-diphenylamine-4-diazo-sulfonic acid
10 parts of 1-(2-hydroxy-naphthalene-3-carbonyl)-amino-3-nitro-benzene
3 parts of sodium hydroxide,

which dyeing preparation yields, when brought onto fibers, by steaming greenish blue dyeings and printings.

10. As a new composition of matter the dyeing preparation consisting of

30 parts of the disodium salt of diphenylamine-4.4'-bis-diazo-sulfonic acid
28, 6 parts of the disodium salt of 1-(2-hydroxy-naphthalene-3-carbonyl)-amino-3-nitro-benzene
8 parts of flowers of sulfur,

which dyeing preparation yields, when brought onto fibers, by steaming black dyeings and printings.

11. A process which comprises applying to vegetable fibers the dyeing preparations claimed in claim 1, drying the fibers thus applied to, steaming and finishing by rinsing and soaping.

12. A process which comprises applying to vegetable fibers the dyeing preparations claimed in claim 2, drying the fibers thus applied to, steaming and finishing by rinsing and soaping.

13. A process which comprises applying to vegetable fibers the dyeing preparations claimed in claim 3, drying the fibers thus applied to, steaming and finishing by rinsing and soaping.

14. A process which comprises applying to vegetable fibers the dyeing preparations claimed in claim 4, drying the fibers thus applied to, steaming and finishing by rinsing and soaping.

15. A process which comprises applying to vegetable fibers the dyeing preparations claimed in claim 5, drying the fibers thus applied to, steaming and finishing by rinsing and soaping.

16. A process which comprises applying to vegetable fibers the dyeing preparations claimed in claim 6, drying the fibers thus applied to, steaming and finishing by rinsing and soaping.

17. A process which comprises applying to vegetables fibers the dyeing preparations claimed in claim 7, drying the fibers thus applied to, steaming and finishing by rinsing and soaping.

18. A process which comprises printing vegetable fibers with a paste containing

20 parts of the sodium salt of 4'-methoxy-diphenylamine-4-diazo-sulfonic acid
15 parts of (2-hydroxy-naphthalene-3-carbonyl-amino)-benzol
20 parts of caustic soda lye of 34° Bé.
4 parts of finely powdered sulfur
20 parts of alcohol
15 parts of Turkey red oil
15 parts of sodium chromate solution 1:4
391 parts of water
500 parts of starch-tragacanth-thickening,

drying the fibers thus imprinted, steaming and finishing by rinsing and soaping.

19. A process which comprises printing vegetable fibers with a paste containing

25, 6 parts of the sodium salt of 4'-methoxy-diphenylamine-4-diazo-sulfonic acid
20 parts of 1-(2-hydroxy-anthracene-3-carbonyl-amino)-2-methyl-benzene
9 parts of caustic soda lye of 34° Bé.
20 parts of thiodiglycol
20 parts of alcohol
405 parts of water
500 parts of starch-tragacanth-thickening,

drying the fibers thus imprinted, steaming and finishing by rinsing and soaping.

20. A process which comprises impregnating vegetable fibers in a bath containing

20 parts of the sodium salt of 4'-methoxy-diphenylamine-4-diazo-sulfonic acid
15 parts of (2-hydroxy-naphthalene-3-carbonyl-amino)-benzene
20 parts of caustic potash lye of 43° Bé.
15 parts of alcohol
15 parts of thiodiglycol
15 parts of sodium chromate solution 1:4
50 parts of mucilage of tragacanth 65:1000
50 parts of water,

drying the fibers thus impregnated, steaming and finishing in the usual manner.

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CERTIFICATE OF CORRECTION.

Patent No. 1,920,542. August 1, 1933.

ARTHUR ZITSCHER, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 51, for "34°" read 43°; page 3, column 1, line 72, for "4-amino-2.4′-dimethoxy-" read 4-amino-2′.4′-dimethoxy-; and line 144, column 5, for "Birght" read Bright; page 5, line 135, claim 20, for "in the usual manner" read by rinsing and soaping; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of November, A. D. 1933.

F. M. Hopkins

(Seal) Acting Commissioner of Patents.