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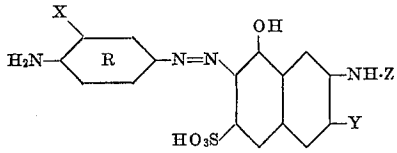
MONOAZO DYESTUFFS SOLUBLE IN WATER

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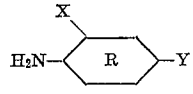
6 Claims. (Cl. 260—198)

The present invention relates to monoazo-dyestuffs soluble in water; more particularly it relates to monoazo-dyestuffs of the following general formula:



wherein X stands for halogen or SO_3H, Y for hydrogen or SO_3H, Z for hydrogen, alkyl or aryl, and wherein the nucleus R may contain further substituents and the dyestuff contains at least two sulfonic acid groups.

We have found that valuable monoazo-dyestuffs soluble in water are obtainable by coupling in an alkaline medium with 2-amino-8-hydroxynaphthalene-6-sulfonic acid or 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid or an N-alkyl or N-aryl derivative thereof, a diazo-compound of the general formula:

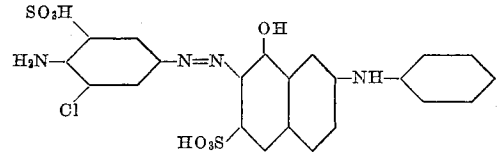


wherein X stands for halogen or the sulfonic acid group, Y stands for a diazo-group and R may contain further substituents, the components being selected in such a manner that the finished dyestuff contains at least two sulfonic acid groups.

The brown dyestuffs thus obtained are particularly adapted for dyeing leather. With regard to their property of dyeing leather in the grain or of dyeing it throughout they are distinctly superior to the water-soluble monoazo-dyestuffs obtainable by coupling in an alkaline solution mono-diazotized 1,3-diamino-4-nitrobenzene with 2-hydroxynaphthalene-3,6-disulfonic acid or diazotized 1-amino-3-acylaminobenzenes, substituted by a nitro-group, with 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid.

The following examples illustrate the invention; the parts are by weight unless otherwise stated; the relationship of parts by weight to parts by volume is that of the kilo to the liter:

(1) 22.25 parts of 2-chloro-1,4-diaminobenzene-6-sulfonic acid in the form of its sodium salt are dissolved in about 100 parts by volume of water together with 6.9 parts of sodium nitrite. This solution is gradually run at 0° C. to 10° C. into 15 parts by volume of crude hydrochloric acid and ice. The suspension of the diazo-compound thus produced is then added in small portions, while stirring and well cooling, to a solution of 32 parts of 2-phenylamino-8-hydroxynaphthalene-6-sulfonic acid in the presence of 38 parts of sodium carbonate in about 200 parts by volume of water. During the coupling operation 100 parts of sodium chloride are gradually added. The precipitated product is filtered by suction and dried; it is a dark-brown powder. The dyestuff corresponding with the following formula:



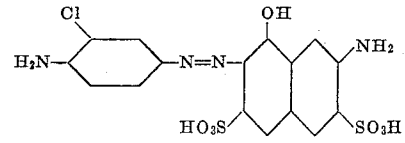
Chrome-tanned calf is neutralized in known manner, well rinsed and dyed at 60° C. for 1 hour with 3 per cent. of the above dyestuff. After addition of formic acid the dyed leather is greased in a fresh bath and finished in the usual manner. It is well dyed in the grain a bluish-brown tint and may be buffed without changing its tint.

By replacing the 22.25 parts of 2-chloro-1,4-diaminobenzene-6-sulfonic acid by the corresponding quantity of 2-bromo-1,4-diaminobenzene-6-sulfonic acid, a dyestuff of similar properties is obtained.

(2) 18.8 parts of 1,4-diaminobenzenesulfonic acid, dissolved in the equivalent amount of dilute caustic soda solution, are suddenly mixed, while cooling, with 25 parts by volume of crude hydrochloric acid. 6.9 parts of sodium nitrite in an aqueous solution are then run in at 0° C. with addition of a stabilizing agent, such as naphthalenesulfonic acid. The filtered diazo-solution is gradually combined with a solution of 24 parts of 2-amino-8-hydroxynaphthalene-6-sulfonic acid in 600 parts by volume of N-sodium carbonate solution. The dyestuff is precipitated with sodium chloride, filtered by suction and dried. It is a dark-brown powder which dyes leather bluish-brown tints.

(3) 14.25 parts of chloro-1,4-diaminobenzene are dissolved in 300 parts of sulfuric acid of 5 per cent. strength and the solution is gradually diazotized at 10° C. to 15° C. with 6.9 parts of sodium nitrite. The filtered diazo-solution is gradually run into a solution of 27.1 parts of 2-amino-8-hydroxynaphthalene-3,6-disulfonic acid in 400 parts by volume of 2N-sodium carbonate solution. The dyestuff is salted out. In the dry state it is a dark-brown powder which dyes

leather well in the grain bluish-brown tints. The dyestuff has the following formula:



(4) By substituting in Example 1 for the 32 parts of 2-phenylamino-8-hydroxynaphthalene-6-sulfonic acid 25.3 parts of 2-methylamino-8-hydroxynaphthalene-6-sulfonic acid and working up the product as usual, a dyestuff of similar properties is obtained.

(5) 20.2 parts of 2-methyl-1.4-diaminobenzene-6-sulfonic acid are diazotized in the usual manner and coupled as described in Example 1 with a solution of 26.7 parts of 2-ethylamino-8-hydroxynaththalene-6-sulfonic acid. The dyestuff, isolated in the usual manner, is a brown powder which dyes leather well in the grain brown tints.

(6) By combining a diazo-solution obtained in the usual manner from 21.8 parts of 2-methoxy-1,4-diaminobenzene-6-sulfonic acid with 35 parts of 2-(4'-methoxyphenylamino)-8-hydroxynaphthalene-6-sulfonic acid, a dyestuff is obtained which dyes leather in the grain bluish-brown tints.

By substituting for the 2-(4'-methoxyphenylamino) - 8 - hydroxynaphthalene - 6 - sulfonic acid 34 parts of 2-(4'-methylphenylamino)-8-hydroxynaphthalene-6-sulfonic acid or 35.5 parts of 2 - (4' - chlorophenylamino) - 8 - hydroxynaphthalene-6-sulfonic acid, dyestuffs of similar properties are obtained.

The following table indicates a number of other azo-dyestuffs which can be made by this invention:

(1) 2,6 - dichloro - 1,4 - diaminobenzene→2-amino - 8 - hydroxynaphthalene - 3,6 - disulfonic acid.

(2) 1,4 - diaminobenzene - 2,6 - disulfonic acid→2 - phenylamino - 8 - hydroxynaphthalene-6-sulfonic acid.

(3) 2,6 - dibromo - 1,4 - diaminobenzene→2 - amino - 8 - hydroxynaphthalene - 3,6 - disulfonic acid.

(4) 2 - ethoxy - 1,4 - diaminobenzene - 6 - sulfonic acid→2 - phenylamino - 8 - hydroxynaphthalene-6-sulfonic acid.

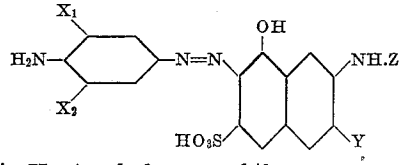
(5) 2 - methoxy - 1,4 - diaminobenzene - 6 - sulfonic acid→2 - phenylamino - 8 - hydroxynaphthalene-6-sulfonic acid.

(6) 2 - methyl - 1,4 - diaminobenzene - 6 - sulfonic acid→2 - phenylamino - 8 - hydroxynaphthalene-6-sulfonic acid.

The dyestuffs obtained penetrate deeply into the leather and yield brown shades.

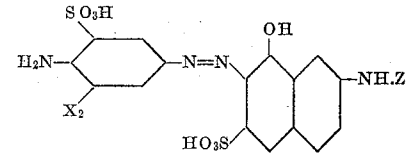
We claim:

1. The monoazo-dyestuffs of the following general formula:



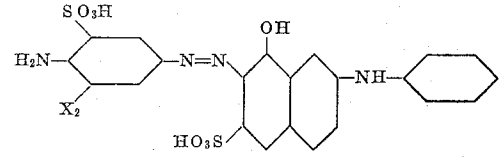
wherein X_1 stands for one of the group consisting of halogen and SO_3H, X_2 for one of the group consisting of hydrogen, halogen, alkyl, alkoxy and SO_3H, Y means a member of the group consisting of hydrogen and SO_3H, and Z a member of the group consisting of hydrogen, alkyl and a radical of the benzene series, and wherein the dyestuff contains at least two sulfonic acid groups, being brown powders, easily soluble in water, penetrating deeply into the leather and yielding brown shades.

2. The monoazo-dyestuffs of the following general formula:



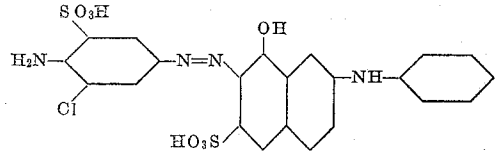
wherein X_2 stands for one of the group consisting of hydrogen, halogen, alkyl, alkoxy and SO_3H and Z means a member of the group consisting of hydrogen, alkyl and a radical of the benzene series, being brown powders, easily soluble in water, penetrating deeply into the leather and yielding brown shades.

3. The monoazo-dyestuffs of the following general formula:



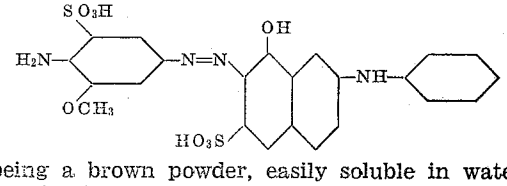
wherein X_2 stands for one of the group consisting of hydrogen, halogen, alkyl, alkoxy and SO_3H, being brown powders, easily soluble in water, penetrating deeply into the leather and yielding brown shades.

4. The monoazo-dyestuff of the following formula:



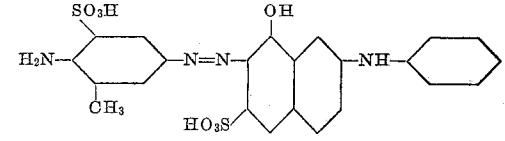
being a dark-brown powder, easily soluble in water, penetrating deeply into the leather and yielding bluish-brown shades.

5. The monoazo-dyestuff of the following formula:



being a brown powder, easily soluble in water, penetrating deeply into the leather and yielding brown shades.

6. The monoazo-dyestuff of the following formula:



being a brown powder, easily soluble in water, penetrating deeply into the leather and yielding brown shades.

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