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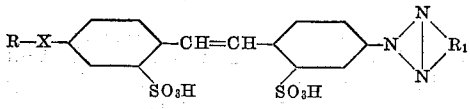
AZODYESTUFFS

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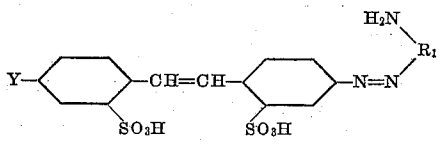
5 Claims. (Cl. 260—44.1)

Our invention relates to new azodyestuffs more particularly to those corresponding to the general formula:



wherein X stands for an azo- or azoxy group, R means a radicle of the benzene or naphthalene series which may be connected with a benzothiazolic or arylazo radicle or the whole radicle attached on the other side to X and R_1 means a radicle of the naphthalene series which may contain a sulfonic or carboxylic acid group or may be connected with a further arylazo group.

The new azodyestuffs are obtained by oxidizing a stilbene compound of the general formula:



wherein Y stands for a nitro or aryl-azo- or aryl-azoxy-group and R_1 has the aforesaid signification, in an alkaline solution, for instance by means of cupric sulfate. In the case of Y standing for a nitro group it is to be converted subsequently into an arylazo- or arylazoxy group.

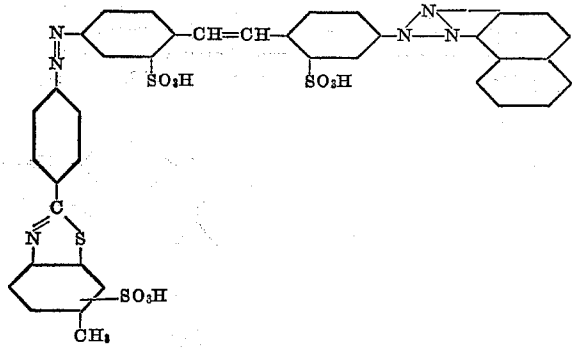
The present new azodyestuffs which may be purified by an aftertreatment usual for stilbene azodyestuffs dye the vegetable fibers yellow to red to brownish shades of a good fastness particularly to light.

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, however, to be understood that our invention is not limited to the examples given nor to the exact conditions stated therein:—

Example 1

The diazo compound of 42.2 parts of 4-nitro-4'-amino-stilbene-2,2'-disulfonic acid is combined with 15 parts of 2-aminonaphthalene in the presence of sodium acetate. The separated paste of the formed ortho-amino-azodyestuff is dissolved in about 1200 parts of water and 30 parts of an aqueous ammonia solution is added. Then at about 100° C. an aqueous solution of 52 parts of crystallized copper sulfate is added, whereby the oxidation to the triazole occurs.

The separated triazole is mixed with 1500 parts of water, 200 parts of a caustic soda solution of 36° Bé. and 32,8 parts of dehydro-thio-toluidine-mono-sulfonic acid and the mixture is boiled for about 24 hours. When cool the separated dyestuff is filtered off, washed out with salt water and dried. The dyestuff of the formula:



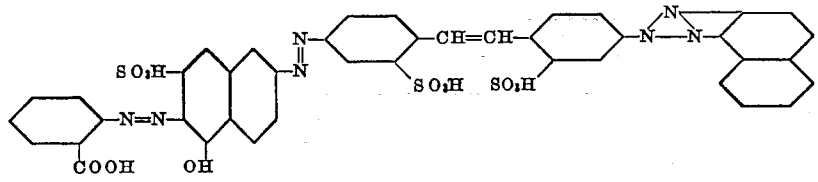
represents a yellowish red powder soluble in water with a yellow, in concentrated sulfuric acid with a bluish red color. It is very well fixed on cotton dyeing yellow shades of a good fastness to light.

When using instead of 2-naphthylamine such naphthylaminomono- or disulfonic or carboxylic acids, which combine with diazocompounds in ortho-position to the amino group and are therefore capable of the formation of the triazolic ring such as 1-aminonaphthalene-4-sulfonic acid, and condensing such azodyestuffs with dehydrothiotoluidine-mono- or disulfonic acid likewise yellow dyestuffs of a good fastness to light are obtained.

Example 2

59.6 parts of the triazolic compound of the dyestuff nitrostilbene-disulfonic acid-azo-2-aminonaphthalene as described in Example 1 are dissolved in about 2000 parts of water. Then a solution of 40,9 parts of the amino-azo-dyestuff, obtained by combining in an alkaline medium diazotized anthranilic acid with 2-amino-5-hydroxy-naphthalene-7-sulfonic acid, in about 1500 parts of water and 450 parts of a caustic soda solution of 36° Bé. are added and the mixture is boiled while stirring for about 24 hours. When cool the separated dyestuff is filtered off, washed out with

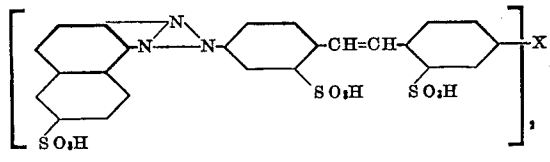
salt water and dried. The new dyestuff of the formula:



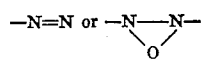
dyes cotton brownish red shades which turn when aftertreated with copper compounds to a reddish brown of a very good fastness to light. If the dyestuff in substance is treated with copper salts according to one of the known methods a copper complex compound is formed well fixing on cotton and dyeing it brownish red shades of a very good fastness to light.

Example 3

The diazo compound of 42.2 parts of nitroaminostilbene-disulfonic acid is combined in the usual manner with 25 parts of 2-aminonaphthalene-6-sulfonic acid. The separated dyestuff is dissolved in a moist state in about 1200 parts of water and 100 parts of a caustic soda solution of 36° Bé. Then 11 parts of glucose are added and the mixture is kept at about 75° C. for some hours. After having neutralized the reaction mass with hydrochloric acid the reduction product is separated, then dissolved in about 1200 parts of water with the addition of 18 parts of sodium carbonate and while boiling the solution is oxidized by means of an aqueous solution of 52 parts of crystallized copper sulfate. The separated cuprous oxide is removed by filtration and from the filtrate the triazolic compound is separated by the addition of common salt. The new dyestuff of the formula:



wherein X means the group



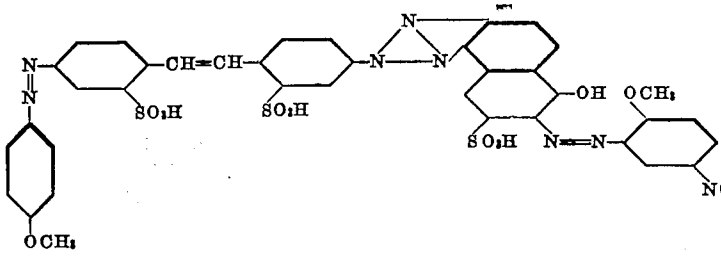
dissolves in water with a yellow, in concentrated sulfuric acid with a reddish violet color. It dyes cotton yellow shades fast to light.

When replacing the 2-aminonaphthalene-6-sulfonic acid by other amino-naphthalene- or naphthol-sulfonic acids which combine in the ortho-position to the amino group and can be oxidized to the triazolic compound, such as 1-aminonaphthalene-4-sulfonic acid or 2-amino-5-hydroxynaphthalene-7-sulfonic acid, 2-amino-8-hydroxy-naphthalene-6-sulfonic acid, yellow dyestuffs are obtained which can be further combined for instance with diazocomponents which contain in the orthoposition to the aminogroup a group capable of forming a metallic complex. The copper complex compounds of these dyestuffs dye cotton brown shades of a very good fastness to light.

Example 4

The azodyestuff obtained by combining diazotized 4-nitro-4'-amino-stilbene-2,2'-disulfonic acid with phenol is methylated and then reduced by means of sodium sulfide. 50.3 parts thereof are diazotized and combined in an acid medium with 27.1 parts of 2-amino-5-hydroxynaphthalene-7-sulfonic acid. When the combination is complete the reaction mass is warmed and the dyestuff is isolated by adding salt and filtered off. The residue is while moist dissolved in about 1000 parts of water with the addition of 30 parts of sodium carbonate. While boiling an aqueous solution of 52 parts of crystallized coper sulfate is added and the mixture is further heated for about an hour. The separated cuprous oxide is filtered off and from the filtrate the triazolic compound is isolated by adding salt. It is then combined with the addition of sodium carbonate with the diazocompound of 16.8 parts of 4-nitro-2-amino-1-anisol.

The new dyestuff of the formula:



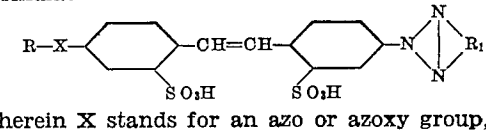
represents when dry a dark brown water soluble powder and dyes cotton brownish red shades turning to reddish brown when aftertreated with copper compounds. The copper complex compound thereof obtainable according to one of the known methods dyes cotton reddish brown shades which are very fast to light.

Similar dyestuffs of brown and reddish brown shades are obtained by replacing the 4-nitro-2-amino-1-anisol by corresponding quantities of other diazocompounds containing in the ortho-position to the aminogroup a group capable of forming a metallic complex.

Instead of the 2-amino-5-hydroxynaphthalene-7-sulfonic acid likewise other suitable aminonaphthol sulfonic acids may be used.

We claim:—

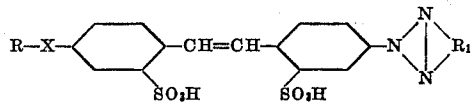
1. Azodyestuffs corresponding to the general formula:



wherein X stands for an azo or azoxy group, R means a radicle of the benzene or naphthalene series which may be connected with a benzothiazolic or arylazo radicle or the whole radicle attached on the other side to X, and R_1 means a

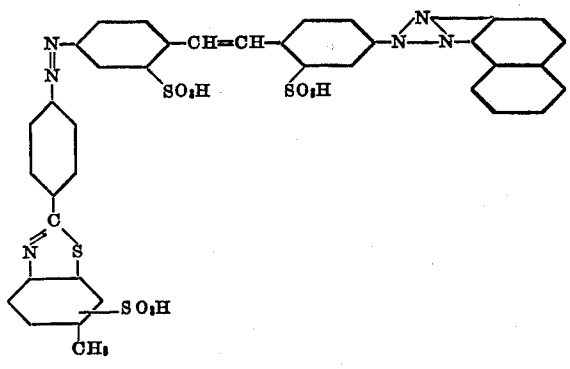
radicle of the naphthalene series which may contain a sulfonic or carboxylic acid group or may be connected with a further arylazo group, which dyestuffs dye the vegetable fibers yellow to red to brownish shades of a good fastness particularly to light.

2. Azodyestuffs corresponding to the general formula:



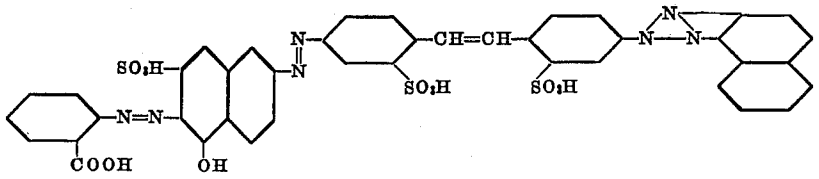
wherein X stands for an azo or azoxy group, R means a radicle of the benzene or naphthalene series which may be connected with a benzothiazolic or arylazo radicle and R_1 means a radicle of the naphthalene series which may contain a sulfonic or carboxylic acid group or may be connected with a further arylazo group, which dyestuffs dye the vegetable fibers yellow to red to brownish shades of a good fastness particularly to light.

3. The azodyestuff of the formula:



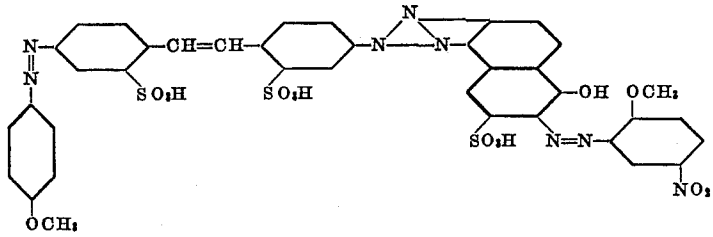
which dyestuff represents when dry a yellowish red powder soluble in water with a yellow, in concentrated sulfuric acid with a bluish red color, which dyestuff dyes cotton yellow shades of a good fastness to light.

4. The azodyestuff of the formula:



which dyestuff dyes cotton brownish red shades which turn when aftertreated with copper compounds to a reddish brown of a very good fastness to light.

5. The azodyestuff of the formula:



which dyestuff represents when dry a dark brown water soluble powder dyeing cotton brownish red shades turning to reddish brown when aftertreated with copper compounds.

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