

## UNITED STATES PATENT OFFICE

2,117,426

## AZO DYES

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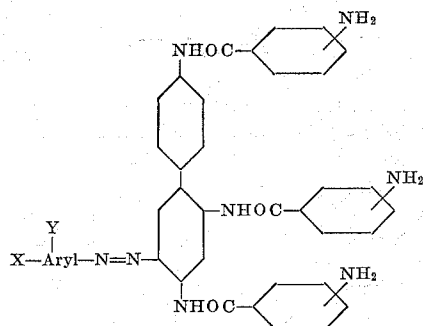
No Drawing. Application July 22, 1937,  
Serial No. 155,042

6 Claims. (Cl. 260—72)

This invention relates to azo dyes. Particularly the invention relates to a method of applying compounds of the type described in Jordan et al. application for "Azo dyes", filed of even date herewith, Serial #155,041 to cellulose, within which term is meant the celluloses and regenerated cellulose.

It is an object of the invention to produce new dyes which have exceptional fastness to washing.

The objects of the invention are accomplished, generally speaking, by diazotizing the compound represented by the formula:



amino, tertiary amino, carboxy, and sulfonic acid, and aryl has a single nucleus from the group consisting of benzene and naphthalene, coupling it to, preferably, beta naphthol, or to other azo dyestuff coupling components.

The following examples illustrate but do not limit the invention. In these examples parts are by weight.

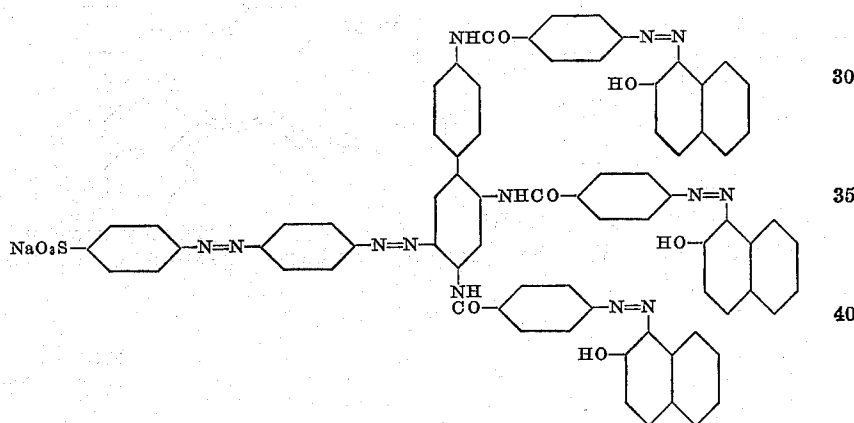
*Example I*

Five tenths part of cotton piece goods are dyed in the usual manner, known to those skilled in the art, with ten hundredths part of

4-amino-azobenzene-4'-sodium-sulfonate→

2-amino-benzidine (PAB)<sub>2</sub>

The dyed fabric is rinsed in cold water and put in 200 parts of water at 20° C. Add three tenths part of sodium nitrite and four tenths part of sulfuric acid. Stir 15 minutes. Rinse with cold water. Dissolve one tenth part of beta-naphthol in 200 parts of water and one twentieth part of caustic soda. Stir the solution rapidly while adding the above rinsed piece goods. Stir 15 minutes. Rinse in cold water and dry. The dyeing is a red orange shade. The probable formula of the dye on the fiber is:

*Example II*

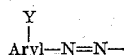
Five tenths part of cotton piece goods is dyed in the usual manner, known to those skilled in the art, with ten hundredths part of

metanilic acid→1,6-Cleve's acid→

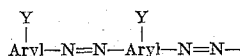
2-amino-benzidine (PAB)<sub>2</sub>

The dyed fabric is rinsed in cold water and put in 200 parts of water at 20° C. Add three tenths part of sodium nitrite and four tenths part of

in which X is one of a group consisting of hydrogen,



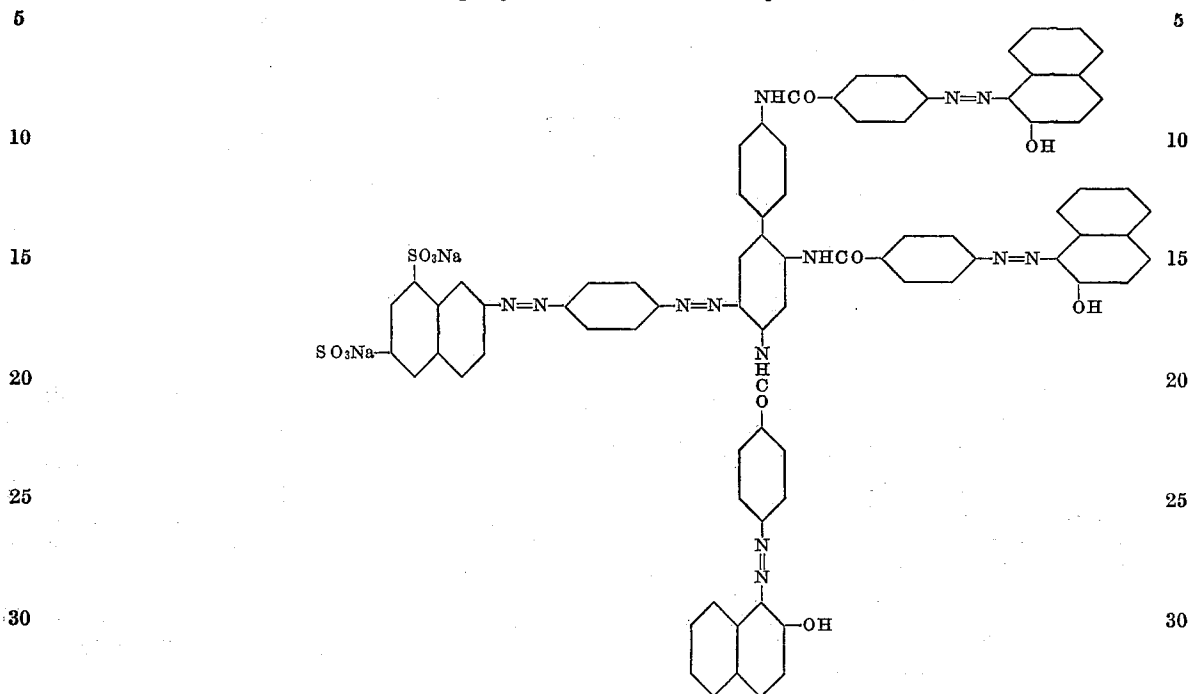
and



Y is at least one of a group consisting of hydrogen, halogen, alkyl, alkoxy, hydroxy, secondary

sulfuric acid. Stir 15 minutes. Rinse with cold water. Dissolve one tenth part of beta-naphthol in 200 parts of water and one twentieth part of caustic soda. Stir the solution rapidly while

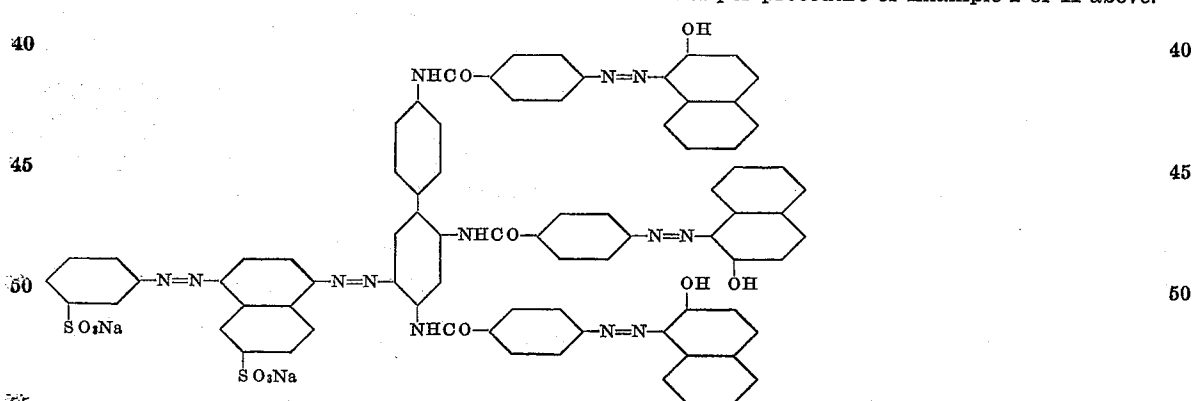
zidine (PAB)<sub>3</sub> when dyed on the fiber and developed with beta-naphthol, as in Example II above, gives a brown shade dyeing. The probable formula of the dyestuff on the fiber is:



adding the above rinsed piece goods. Stir 15 minutes. Rinse in cold water and dry. The dyeing is a brown shade. The probable formula of the dye on the fiber is:

#### Example IV

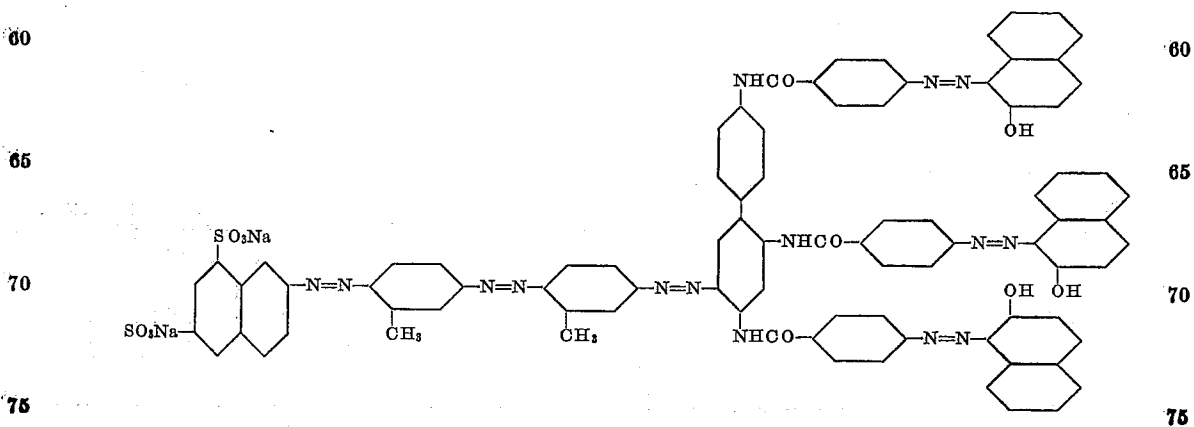
The dye amino G salt→meta-toluidine→meta-toluidine→2-amino-benzidine (PAB)<sub>3</sub> is dyed on the fiber per procedure of Example I or II above.



#### Example III

The dye amino G salt→aniline→2-amino-ben-

It gives a yellow brown shade dyeing. The probable formula of the dye on the fiber is:



In the following table are other examples illustrating the invention: wise their insolubility renders them of comparatively little use.

Ex.	Diazo component	Coupling component	Shade on cellulose	
5				5
5	Sulfanilic acid $\rightarrow$ 2-amino-5-hydroxy-naphthalene-7-sulfonic acid $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	Beta-naphthol	Red brown.	
6	Sulfanilic acid $\rightarrow$ 2-amino-5-hydroxy-naphthalene-7-sulfonic acid $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	1-phenyl-3-methyl-5-pyrazolone.	Yellow brown.	
7	Sulfanilic acid $\rightarrow$ 2-amino-5-hydroxy-naphthalene-7-sulfonic acid $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	Acetoacet-anilide	Do.	10
8	Sulfanilic acid $\rightarrow$ 2-amino-5-hydroxy-naphthalene-7-sulfonic acid $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	Meta-tolylene diamine	Red brown.	
9	4-Amino-azobenzene-4'-sodium-sulfonate $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	Beta-naphthol	Red orange.	
10	2-Naphthylamine-6, 8-disulfonic acid $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	do	Bordeaux.	15
11	2-Naphthylamine-6, 8-disulfonic acid $\rightarrow$ cresidine $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	do	Brown.	
12	Metanilic acid $\rightarrow$ 1, 6-Cleve's acid $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	do	Do.	
13	8-Amino-1-naphthol-3, 6-disulfonic acid $\rightarrow$ cresidine $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	do	Violet.	
14	Sulfanilic acid $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	do	Brown.	20
15	2-Naphthylamine-6, 8-disulfonic acid $\rightarrow$ aniline $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	do	Do.	
16	2-Naphthylamine-6, 8-disulfonic acid $\rightarrow$ meta-toluidine $\rightarrow$ meta-toluidine $\rightarrow$ 2-amino-benzidine (PAB) <sub>3</sub> .	do	Yellow brown.	

In the above table (PAB) stands for (para-amino-benzoyl).

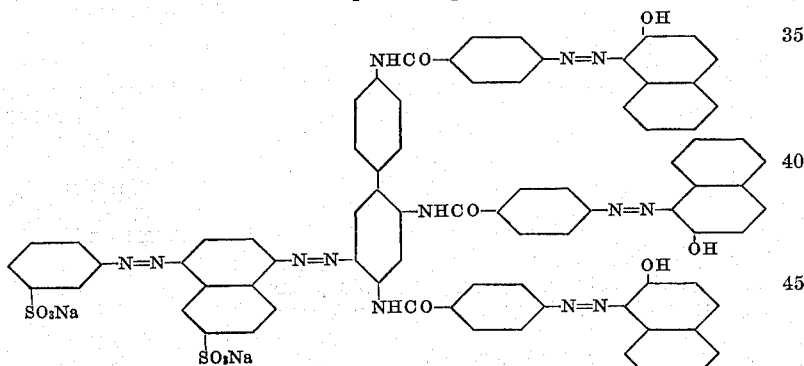
The preferred coupling components are beta-naphthol and 1-phenyl-3-methyl-5-pyrazolone. Less desirably, however, but still usefully, acetoacet-anilide and meta-tolylene-diamine may be used.

To be of greatest advantage the products of this invention should be produced on the fiber, other-

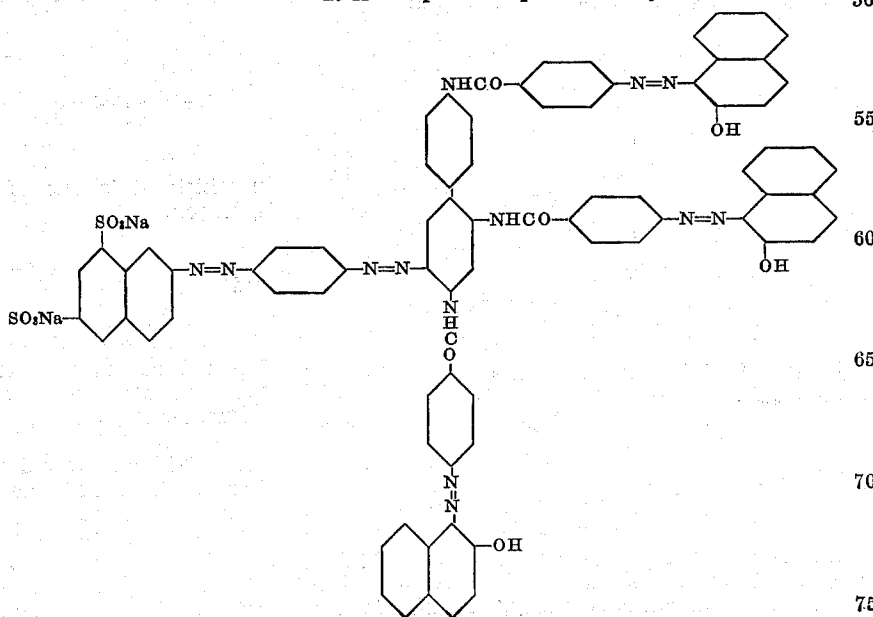
As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

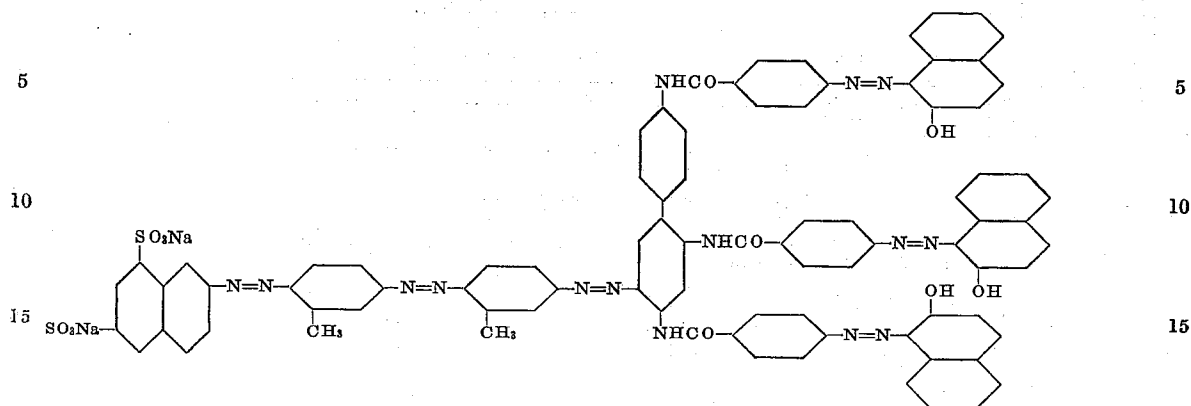
1. A compound represented by the formula:



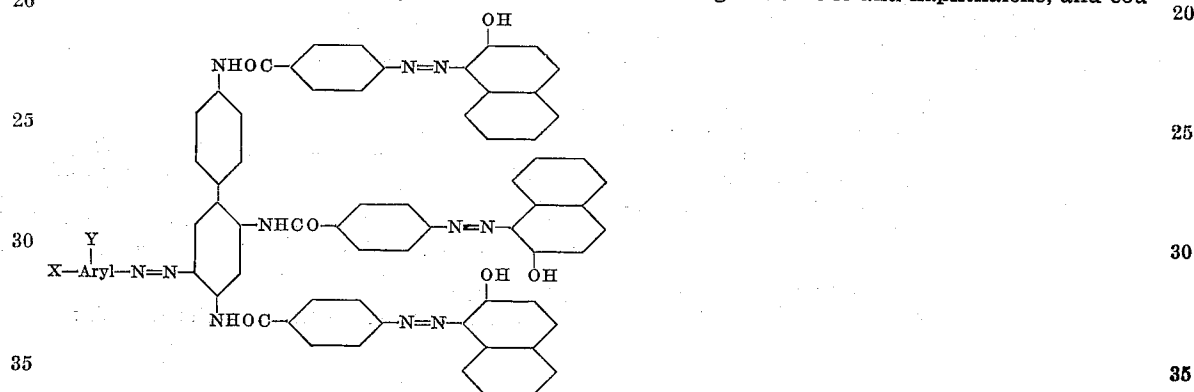
2. A compound represented by the formula:



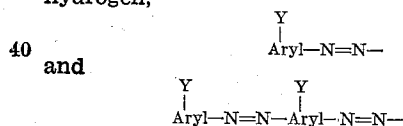
3. A compound represented by the formula: and aryl has a single nucleus from the group



4. A compound represented by the formula: consisting of benzene and naphthalene, and cou-

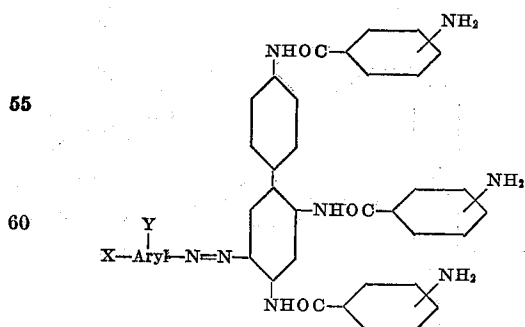


in which X is one of a group consisting of hydrogen,

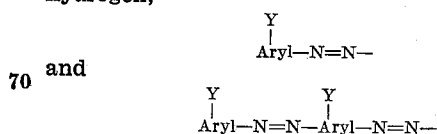


Y is at least one of a group consisting of hydrogen, halogen, alkyl, alkoxy, hydroxy, secondary amino, tertiary amino, carboxy, and sulfonic acid, and aryl has a single nucleus from the group consisting of benzene and naphthalene.

5. The process which comprises diazotizing a compound represented by the formula:



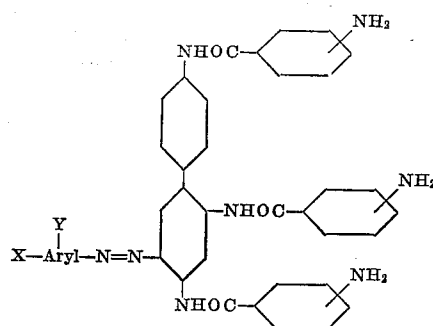
in which X is one of a group consisting of hydrogen,



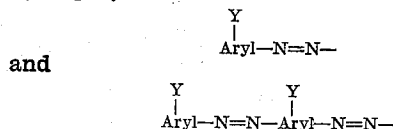
Y is at least one of a group consisting of hydrogen, halogen, alkyl, alkoxy, hydroxy, secondary amino, tertiary amino, carboxy, and sulfonic acid,

pling it with a compound from the group consisting of beta-naphthol, meta-tolylene-diamine, 1-phenyl-3-methyl-5-pyrazolone, and acetoacet-aniline.

6. Cellulose dyed with the product produced by impregnating the cellulose with the compound represented by the formula:



in which X is one of a group consisting of hydrogen,



Y is at least one of a group consisting of hydrogen, halogen, alkyl, alkoxy, hydroxy, secondary amino, tertiary amino, carboxy, and sulfonic acid, and aryl has a single nucleus from the group consisting of benzene and naphthalene, diazotizing it on the fiber, and coupling it to one of a group of compounds consisting of beta-naphthol, meta-tolylene-diamine, 1-phenyl-3-methyl-5-pyrazolone, and acetoacet-anilide.

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