

## UNITED STATES PATENT OFFICE

2,406,004

## MONOAZO COMPOUNDS

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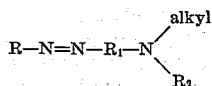
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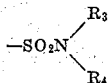
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This invention relates to new azo dye compounds and their application to the art of dyeing.

We have discovered that dyeings which can be discharged to a clear white can be obtained by dyeing a suitable textile material with a dye having the formula:



wherein R stands for the residue of a benzene nucleus containing an  $\text{NH}_2$  group in para position to the azo bond shown and a



group, wherein  $\text{R}_3$  stands for a member selected from the group consisting of hydrogen and an alkyl group and  $\text{R}_4$  stands for a member selected from the group consisting of an alkyl group and a benzene nucleus, in ortho or meta position to the azo bond shown,  $\text{R}_1$  stands for the residue of a benzene nucleus and  $\text{R}_2$  stands for a member selected from the group consisting of an alkyl group and a benzene nucleus, diazotizing the dye on the fiber and developing with a developer component.

So far as we are aware both the monoazo dye compounds and the disazo dye compounds resulting from the development operation constitute new compounds. Accordingly, it is an object of our invention to provide new azo dye compounds. Another object is to provide dyeings on textile materials which are of good fastness to light and washing and which can be discharged to a clear white. A particular object is to provide cellulose acetate textile materials dyed navy blue or black shades of good fastness to light and washing and which are dischargeable to a clear white.

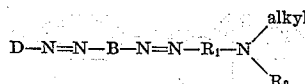
The dyeing process of our invention appears to be particularly of value in connection with the production of navy blue to black shades on cellulose acetate textile materials. However, the dye compounds of our invention are applicable to the coloration of organic derivatives of cellulose in general as well as to other textile materials such as nylon, wool and silk. Our invention seems to be of greatest utility in connection with the coloration of cellulose acetate and nylon textile materials.

Typical organic derivatives of cellulose include the hydrolyzed as well as the unhydrolyzed cellulose organic acid esters such as cellulose ace-

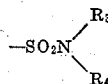
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tate, cellulose formate, cellulose propionate or cellulose butyrate and the hydrolyzed as well as the unhydrolyzed mixed organic acid esters of cellulose such as cellulose acetate-propionate, cellulose acetate-butyrate and the cellulose ethers such as methyl cellulose, ethyl cellulose or benzyl cellulose. While our invention will be described more particularly in connection with the dyeing of cellulose acetate silk, it will be understood that it is applicable to the dyeing of the other textile materials which have been indicated hereinbefore.

Depending upon the particular developer component used to develop the diazotized dye on the fiber yellow, scarlet, violet, navy blue and black dyeings can be obtained. The use of components, such as 2-hydroxy-3-carboxynaphthalene, yielding dischargeable navy blue to black shades appears to be of greatest importance since these shades are in demand and dyes which can yield them are highly desirable. The disazo dyes resulting from the development operation have the formula:



wherein D stands for the residue of a developer component, B stands for the residue of a benzene nucleus containing a



group and wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  have the meaning previously assigned to them.

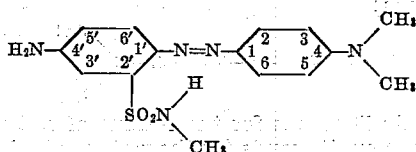
The dye compounds of our invention possess properties which make them of unusual industrial importance. The free amino dye compounds combine good speed of dyeing with good exhaustion and for the most part can be applied to the fiber at a temperature as low as  $60^\circ \text{C}$ . Further, generally speaking, these free amino dye compounds possess good solubility in water and do not gum on heating with steam. When diazotized on the fiber and coupled with a developer component, such as 2-hydroxy-3-carboxynaphthalene, desirable shades of color are obtained which are of good fastness to light and washing and which are readily dischargeable to a clear white. Ready dischargeability to a clear white is a very important property for a dye to possess.

The qualities above enumerated, as previously noted, make the dye compounds of our invention very valuable commercially. Rapid dyeing

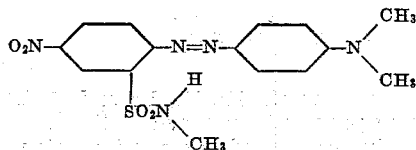
at low temperatures coupled with good exhaustion are qualities of utmost importance in jig dyeing operations which normally are conducted at temperatures of 60-65° C. Thus dye compounds, which dye rapidly at temperatures of 80-85° C. and which are otherwise satisfactory but which possess poor affinity for the fiber at 60-65° C. have little or no utility for present day commercial jig dyeing operations. Accordingly, the discovery of dye compounds which dye rapidly at low temperatures, which exhaust well, which have excellent solubility in water, which do not form gummy deposits and which yield dyeings of excellent fastness to light and washing and which are readily dischargeable to white constitutes an important as well as unexpected technological advance.

Concentrations, for example, from 1/4% to 3% by weight of the dye to the material undergoing dyeing can be employed in the initial dyeing operation, pretty orange-yellow dyeings being obtained. For the development operation following the diazotization of the free amino dye compound on the fiber, an excess of the developer component is ordinarily employed. The intensity of shade obtained varies depending on the amount of the free amino dye absorbed by the fiber in the initial dyeing operation. To illustrate, when 2-hydroxy-3-carboxynaphthalene is the developer component at lower concentrations, the color appears navy blue but as the concentration increases the intensity of the color increases until the color appears black. Thus it is seen that the intensity of the shade increases with an increase in the amount of the free amino dye applied to the fiber.

The monoazo dye compounds of our invention can be prepared by reducing the corresponding nitro dye compounds to the free amino form. Thus 4'-amino-2'-sulfonemethylamidobenzeneazo-4-dimethylaminobenzene having the formula:



can be prepared by reducing



The preparation of the monoazo nitro compounds is illustrated in our U. S. Patent 2,261,175, issued November 4, 1941, wherein a considerable number of such compounds is disclosed.

The following examples illustrate the invention:

#### Example 1

17.7 grams of 4'-nitro-2'-sulfonemethylamidobenzeneazo-4-dimethylaminobenzene are heated in 100 cc. of ethyl alcohol to boiling. A solution of 8 grams of 60% sodium sulfide fused with 2 grams of sulfur in 20 cc. of water is then added in small portions because the reduction reaction which takes place is very vigorous. After all of the sulfide reaction mixture has been added, the resulting reaction mixture is refluxed for 45-60 minutes after which it is poured through a filter paper into two liters of cold water which is stirred vigorously. Vigorous stirring is required because

the dye compound formed tends to coagulate as a gummy mass unless it is well stirred to keep the product broken up. 11.3 grams, which is 67.45% of the theoretical yield of 4'-amino-2'-sulfonemethylamidobenzeneazo-4-dimethylaminobenzene is obtained in the form of small finely formed red-orange crystals. The dye compound formed is recovered by filtration, washed with water and dried.

By substituting an equivalent gram molecular weight of 4'-nitro-2'-sulfonemethylamidobenzeneazo-4-diethylaminobenzene for the starting dye compound of the example 4'-amino-2'-sulfonemethylamidobenzeneazo-4-diethylaminobenzene is obtained. This dye compound is likewise obtained as red-orange crystals and has properties substantially the same as the dye compound of the example.

#### Example 2

23 grams of 4'-nitro-2'-sulfonemethylamidobenzeneazo-4-di-β-hydroxyethylaminobenzene are heated in 100 cc. of ethyl alcohol in a reaction vessel to boiling. A solution of 8 grams of fused 60% sodium sulfide in 18 cc. of water is then added in small portions because the reduction reaction proceeds very vigorously. After all of the sulfide solution has been added, the reaction mixture is boiled for 45-60 minutes and then poured through a filter paper into two liters of cold water which is vigorously stirred. 13 grams, which is 65% of the theoretical amount of 4'-amino-2'-sulfonemethylamidobenzeneazo-4-di-β-hydroxyethylaminobenzene is recovered by filtration as well formed orange crystals. The dye compound obtained is washed with water and dried.

#### Example 3

23.9 grams of 4'-nitro-2'-sulfonemethylamidobenzeneazo-2-chloro-4-(ethyl, β-hydroxyethyl)aminobenzene are placed in a reaction vessel together with 200 cc. of ethyl alcohol and the mixture resulting is heated to boiling. 8 grams of fused 60% sodium sulfide in 18 cc. of water is then added in small portions to prevent the reduction reaction from being too vigorous. After all of the sulfide solution has been added the reaction mixture is refluxed for 45-60 minutes and then poured through a filter paper into 2 liters of cold water which is being stirred vigorously. 17.5 grams, which is 82% of the theoretical amount of 4'-amino-2'-sulfonemethylamidobenzeneazo-2-chloro-4-(ethyl, β-hydroxyethyl)aminobenzene is obtained after filtration of the reaction mixture in the form of well formed red-orange crystals. The dye compound obtained is washed with water and dried.

Following the procedure described in Examples 1, 2 and 3, the following monoazo dyes of our invention can be prepared. In naming the dye compounds tabulated hereinafter, the numbering indicated in connection with the dye 4'-amino-2'-sulfonemethylamidobenzeneazo-4-dimethylaminobenzene has been followed.

1. 4'-amino-2'-sulfone-β-hydroxyethylamidobenzeneazo-4-dimethylaminobenzene.
2. 4'-amino-2'-sulfone-β-methoxyethylamidobenzeneazo-4-dimethylaminobenzene.
3. 4'-amino-2'-sulfone-β-methoxyethylamidobenzeneazo-4-diethylaminobenzene.
4. 4'-amino-2'-sulfone-β-methoxyethylamidobenzeneazo-4-(ethyl, β-hydroxyethyl)aminobenzene.
5. 4'-amino-2'-sulfone-β-methoxyethylamidobenzeneazo-4-di-β-hydroxyethylaminobenzene.

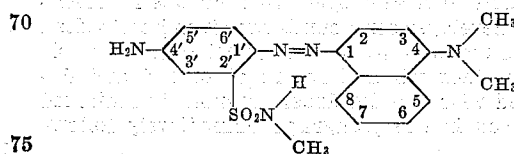
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6. 4' - amino-2'-sulfone- $\beta$ -methoxyethylamido-benzeneazo-4-di- $\beta$ -hydroxypropylaminobenzene.
7. 4' - amino-3'-sulfonethylamidobenzeneazo-4-di- $\beta$ -hydroxyethylaminobenzene.
8. 4' - amino-3'-sulfonephenylamidobenzeneazo-4-di- $\beta$ -hydroxyethylaminobenzene.
9. 4' - amino-3'-sulfone- $\beta$ -hydroxyethylamido-benzeneazo-4-di- $\beta$ -hydroxyethylaminobenzene.
10. 4' - amino-3'-sulfonemethylamidobenzeneazo-4-di- $\beta$ -hydroxyethylaminobenzene.
11. 4'-amino-3'-sulfone- $\beta$ -methoxyethylamido-benzeneazo-4-di- $\beta$ -hydroxyethylaminobenzene.
12. 4' - amino-3'-sulfonethylamidobenzeneazo-4-dimethylaminobenzene.
13. 4' - amino-3'-sulfonethylamidobenzeneazo-4-(methyl, phenyl) - aminobenzene.
14. 4' - amino-3'-sulfonethylamidobenzeneazo-4-(ethyl,  $\beta$ , $\gamma$ -dihydroxypropyl) - aminobenzene.
15. 4' - amino - 2' - sulfonephenylamidobenzenaeazo-4-di- $\beta$ -hydroxyethylaminobenzene.
16. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-4-(methyl, phenyl) - aminobenzene.
17. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-2-acetamino-4-diethylaminobenzene.
18. 4' - amino - 2' - sulfonemethylamidobenzenaeazo - 2 - methyl-5-methoxy-4-di- $\beta$ -hydroxyethylaminobenzene.
19. 4' - amino - 2' - sulfonemethylamidobenzenaeazo - 2 - acetamino - 5 - ethoxy-4-di- $\beta$ -hydroxyethylaminobenzene.
20. 4' - amino-6'-chloro-2'-sulfonethylamidobenzenaeazo-4-di- $\beta$ -hydroxyethylaminobenzene.
21. 4' - amino - 6' - bromo-2'-sulfonemethylamidobenzenaeazo-4-dipropylaminobenzene.
22. 4' - amino - 6' - methyl-2'-sulfonemethylamidobenzenaeazo - 4 - di- $\beta$ -hydroxyethylaminobenzene.
23. 4' - amino-6'-methoxy-2'-sulfonemethylamidobenzenaeazo-4-dimethylaminobenzene.
24. 4' - amino-6'-chloro-3'-sulfonethylamidobenzenaeazo-4-di- $\beta$ -hydroxyethylaminobenzene.
25. 4' - amino - 5' - methyl-3'-sulfonemethylamidobenzenaeazo-4-dimethylaminobenzene.
26. 4' - amino - 6' - methyl-3'-sulfonemethylamidobenzenaeazo - 4 - (butyl,  $\beta$ -hydroxyethyl) - aminobenzene.
27. 4' - amino - 2' - sulfonephenylamidobenzenaeazo-4-dimethylaminobenzene.
28. 4' - amino - 2' - sulfonephenylamidobenzenaeazo-4-di- $\beta$ -hydroxypropylaminobenzene.
29. 4' - amino - 2' - sulfonedimethylamidobenzenaeazo-4-dimethylaminobenzene.
30. 4' - amino - 2' - sulfonedimethylamidobenzenaeazo-4-(ethyl,  $\beta$ , $\gamma$ -dihydroxypropyl) - aminobenzene.
31. 4' - amino - 2' - sulfonedimethylamidobenzenaeazo-4-di- $\beta$ -hydroxyethylaminobenzene.
32. 4' - amino-2'-sulfonethylamidobenzenaeazo-4-dimethylaminobenzene.
33. 4' - amino-2'-sulfonethylamidobenzenaeazo-4-diethylaminobenzene.
34. 4' - amino-2'-sulfonethylamidobenzenaeazo-4-(ethyl,  $\beta$ -hydroxyethyl) - aminobenzene.
35. 4' - amino-2'-sulfonethylamidobenzenaeazo-4-(ethyl,  $\beta$ , $\gamma$ -dihydroxypropyl) - aminobenzene.
36. 4' - amino-2'-sulfonethylamidobenzenaeazo-4-di- $\beta$ -hydroxypropylaminobenzene.
37. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-4-(ethyl,  $\beta$ -hydroxyethyl) - aminobenzene.
38. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-4-di- $\beta$ -hydroxyethylaminobenzene.
39. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-4-(ethyl,  $\beta$ -hydroxypropyl) - aminobenzene.

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40. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-4-di- $\beta$ -hydroxypropylaminobenzene.
41. 4' - amino-2'-sulfonethylamidobenzenaeazo-4-(butyl,  $\beta$ , $\gamma$ -dihydroxypropyl) - aminobenzene.
42. 4' - amino - 2' - sulfonethylamidobenzenaeazo-4-(ethyl, phenyl) - aminobenzene.
43. 4'-amino-2'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo-4-diethylaminobenzene.
44. 4'-amino-2'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo-4-dibutylaminobenzene.
45. 4'-amino-2'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo-4-di- $\beta$ -hydroxypropylaminobenzene.
46. 4'-amino-2'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo-4-di- $\beta$ -hydroxyethylaminobenzene.
47. 4'-amino-2'-sulfone- $\beta$ -methoxyethylamidobenzenaeazo-4-dimethylaminobenzene.
48. 4'-amino-2'-sulfone- $\beta$ -methoxyethylamidobenzenaeazo - 4 - (ethyl,  $\beta$ , $\gamma$  - dihydroxypropyl) - aminobenzene.
49. 4'-amino-2'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo-4-(methyl, propyl) - aminobenzene.
50. 4'-amino-2'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo-4-(butyl,  $\beta$ -hydroxyethyl) - aminobenzene.
51. 4'-amino-2'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo-4-(isoamyl,  $\beta$ -hydroxyethyl) - aminobenzene.
52. 4'-amino-2'-sulfonebutylamidobenzenaeazo-4-diethylaminobenzene.
53. 4'-amino-2'-sulfonebutylamidobenzenaeazo-4-dimethylaminobenzene.
54. 4' - amino - 2' - sulfonedi- $\beta$ -hydroxyethylamidobenzenaeazo-4-dimethylaminobenzene.
55. 4'-amino-2'-sulfonedi -  $\beta$  - hydroxyethylamidobenzenaeazo-4-diethylaminobenzene.
56. 4'-amino - 2' - sulfonemethylamidobenzenaeazo-2-sulfonethylamido-4-di -  $\beta$  - hydroxyethylaminobenzene.
57. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-2-methyl-4-diethylaminobenzene.
58. 4' - amino - 2' - sulfonemethylamidobenzenaeazo-4-dimethylaminonaphthalene.
59. 4' - amino-2'-sulfonethylamidobenzenaeazo-4-di- $\beta$ -hydroxyethylaminonaphthalene.
60. 4' - amino - 2' - sulfonephenylamidobenzenaeazo-4-(ethyl,  $\beta$ -hydroxyethyl) - aminonaphthalene.
61. 4'-amino-2'-sulfone- $\beta$ -methoxyethylamidobenzenaeazo-4-(methyl,  $\gamma$ -hydroxypropyl) - aminonaphthalene.
62. 4' - amino - 2' - sulfonedimethylamidobenzenaeazo-4-(ethyl,  $\beta$ , $\gamma$ -dihydroxypropyl) - aminonaphthalene.
63. 4'-amino-6'-chloro-2'-sulfonepropylamidobenzenaeazo-4-butylaminonaphthalene.
64. 4' - amino - 3' - sulfonemethylamidobenzenaeazo-4-dimethylaminonaphthalene.
65. 4'-amino-3'-sulfone- $\beta$ -hydroxyethylamidobenzenaeazo - 4 - di- $\beta$ -methoxyethylaminonaphthalene.
66. 4' - amino-3'-sulfonethylamidobenzenaeazo-4-(butyl, phenyl) - aminonaphthalene.

The numbering used in naming the monoazo dyes above tabulated which contain a naphthalene nucleus will be clear from 4'-amino-2'-sulfonemethylamidobenzenaeazo - 4 - dimethylaminonaphthalene which has the formula:



While a considerable number of compounds illustrating the monoazo dye compounds of our invention have been given, it is to be clearly understood that the compounds disclosed are illustrative and not limitative of the invention. Thus, any of the nitrobenzene-sulfonamide compounds disclosed herein can be diazotized and coupled with any of the coupling components indicated herein to yield monoazo dyes which can be converted in accordance with the procedure described in Examples 1, 2 and 3 to yield the monoazo dye compounds of our invention.

The monoazo dye compounds of the invention can be applied to the textile material such as an organic derivative of cellulose textile material by methods well known in the art. They may be applied, for example, from an aqueous solution or suspension of the dye or dyes. In this method the dye is finely ground and ordinarily intimately admixed with a dispersing or solubilizing agent such as soap, sodium sulforicmoleic acid or sodium lignin sulfonate and dispersed in water to form an aqueous dyebath. The material to be dyed is then added to the dyebath thus prepared and dyeing is conducted at a temperature of 60-85° C. until complete. In accordance with the usual dyeing practice, the material to be dyed will ordinarily be added to the dyebath at a temperature lower than that at which the main portion of the dyeing is to be effected, a temperature approximating 45-55° C., for example, following which the temperature of the dyebath is raised to that selected for carrying out the dyeing operation. Usually one to two hours is sufficient for the dyeing operation. As this method of dyeing and modifications of it are well known to those skilled in the art to which this invention is directed, further discussion is believed unnecessary.

The monoazo dye compounds of the invention are principally of importance in connection with so-called developed dyeing operations. In this method of dyeing the monoazo dye (or dyes) is diazotized on the fiber and the diazonium compound resulting is coupled with a compound known as a developer compound. These latter compounds are well known to those skilled in the art as a considerable number of them are disclosed in the prior art. Representative developer compounds are given hereinafter but no attempt has been made to give an exhaustive list. It will be apparent that compounds of the general character as those indicated can also be employed.

Developer compounds that can be employed include 2-hydroxy - 3 - carboxynaphthalene, 1-phenyl-3-methyl-5-pyrazolone, phenol, a cresol such as p-cresol,  $\beta$ -naphthol, arylamides of 2-hydroxy-3-carboxynaphthalene such as the anilide, the m-nitroanilide or the p-methoxyanilide derivatives, 1 - di -  $\beta$  - hydroxyethylamino - 2-methoxy-5-methylbenzene, N-di- $\beta$ -hydroxyethylaminobenzene, N-(ethyl,  $\beta$ -hydroxyethyl)-aminobenzene, N- $\beta$ , $\gamma$ -dihydroxypropyltetrahydroquinoline, 1- $\beta$ , $\gamma$ -dihydroxypropyl-2-methyltetrahydroquinoline and 1- $\beta$ -hydroxyethyl-2,7 - dimethyltetrahydroquinoline.

The colors obtainable when representative monoazo dyes of our invention are applied to cellulose acetate textile materials, diazotized on the fiber and then developed with various representative developer compounds are given hereinafter. Twelve monoazo dyes are first listed and the colors obtained when they are diazotized and developed with the developer compounds indicated are given in the paragraph immediately following.

1. 4' - amino - 2' - sulfonemethylamidobenzenazo-4-dimethylaminobenzene.

2. 4' - amino - 2' - sulfonemethylamidobenzeneazo-4-di- $\beta$ -hydroxyethylaminobenzene.

3. 4' - amino - 2' - sulfonemethylamidobenzeneazo - 2 - chloro-4-(ethyl,  $\beta$ -hydroxyethyl)-aminobenzene.

4. 4' - amino - 2' - sulfonemethylamidobenzenazo-4-diethylaminobenzene.

5. 4' - amino - 2' - sulfonemethylamidobenzenazo - 4 - (ethyl,  $\beta$  - hydroxyethyl) - aminobenzene.

6. 4' - amino - 3' - sulfonemethylamidobenzeneazo-4-dimethylaminobenzene.

7. 4' - amino - 3' - sulfonemethylamidobenzeneazo-4-di- $\beta$ -hydroxyethylaminobenzene.

8. 4' - amino - 3' - sulfonemethylamidobenzeneazo-4-(methyl, phenyl)-aminobenzene.

9. 4' - amino - 3' - sulfonemethylamidobenzeneazo-4-di- $\beta$ -hydroxyethylaminonaphthalene.

10. 4' - amino - 2' - sulfonemethylamidobenzeneazo-4-di- $\beta$ -hydroxyethylaminonaphthalene.

11. 4' - amino - 6' - chloro - 2' - sulfonemethylamidobenzenazo-4-dimethylaminobenzene.

12. 4' - amino - 2' - sulfonemethylamidobenzenazo-4-di- $\beta$ -methoxyethylaminobenzene.

When the above compounds are diazotized and coupled with 2-hydroxy-3-carboxynaphthalene, navy blue to black dyeings are obtained; when coupled with 1-phenyl-3-methyl-5-pyrazolone, yellow dyeings are obtained; when coupled with  $\beta$ -naphthol, scarlet dyeings are obtained; when coupled with 1-di- $\beta$ -hydroxyethylamino-2-methoxy-5-methylbenzene, violet dyeings are obtained and when 1- $\beta$ , $\gamma$ -dihydroxypropyl-2-methyltetrahydroquinoline is the developer component navy blue dyeings are obtained.

The monoazo dye on the fiber can be diazotized in accordance with the procedure described hereinafter. It will be understood, however, that any other suitable method can be used.

#### *Diazotization of the monoazo dye on the fiber*

After the material has been rinsed after dyeing, it is diazotized in a bath made up as follows: For each 10 grams of cloth, one gram of sodium nitrite is dissolved in a mixture containing 2 grams of concentrated (35%) hydrochloric acid and 300 cc. of water. The diazotization treatment is given for 30-45 minutes at a temperature of about 20° C. Upon completion of the diazotization reaction, the fabric is removed and thoroughly rinsed with water following which it is ready for development.

The development operation of the invention will be illustrated in connection with 2-hydroxy-3-carboxynaphthalene. Generally speaking, the developing operation will be carried out in a moderately acid medium although in certain cases it may be deemed more desirable to carry out the development operation in a slightly alkaline medium.

Following the diazotization treatment, the material is developed, preferably immediately, in a bath made up as follows: for every 10 grams of cloth, 10 cc. of a 5% stock solution of 2-hydroxy-3-naphthoic acid and 1 cc. of glacial acetic acid are added to 300 cc. of water. The stock solution of 2-hydroxy-3-naphthoic acid is made by dissolving 10 grams of 2-hydroxy-3-naphthoic acid in 100 cc. of 5% NaOH and then adding 100 cc. of water. The cellulose acetate cloth from the diazotization treatment is entered in the developing bath at 30° C. and the temperature is gradually raised to 60° C. over a 30 minute pe-

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riod at which temperature the bath is kept for another 30 minutes. Following this treatment, the cellulose acetate silk is removed, washed well with water and dried.

The developing bath made up as described above has a pH of approximately 4.0. By increasing the amount of acetic acid, the pH will be lowered and the shade obtained on the fabric will be greener. If the pH is raised by decreasing the amount of acid added a redder shade is obtained. Using the above procedure, navy blue to black shades can be obtained depending upon the concentration of the monoazo dye on the fiber. The colors obtained are readily discharged to substantially a pure white by the usual reduction discharges such as, for example, the monozinc salt of the formaldehyde sulfoxylic acid (Rongalite).

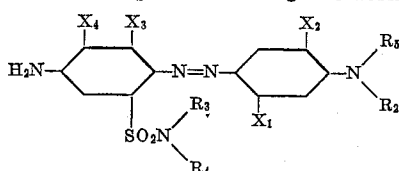
While the development operation has been illustrated in connection with the use of 2-hydroxy-3-carboxynaphthalene, it will be understood that it can be carried out in a similar manner using one of the other developer components indicated herein. That is, the pH of the developer bath can be about 4.0 although as previously indicated the pH is not restricted to this value. The shade obtained will vary somewhat depending upon the pH of the developer bath. If desired, the dyeing can be topped by treating with a direct dye of another shade. Also the development operation can be effected using more than one developer compound. To illustrate, the diazotized fiber can be developed with both 2-hydroxy-3-carboxynaphthalene and 1-phenyl-3-methyl-5-pyrazolone at the same time.

Although the use of the dye compounds of our invention has been described more particularly in connection with cellulose acetate, it will be understood that they can be applied to the other textile materials named herein by the methods described or by methods similar thereto. Further, while the disazo dye compounds of our invention have been shown as being prepared on the fiber, it will be understood that the diazotized monoazo dyes can be coupled with the developer components without being applied to the fiber and if this is done the disazo dyes are obtained per se. Normally the disazo dye is formed on the fiber.

Coupling components wherein the benzene or naphthalene nucleus contains an amino group which is substituted with a phosphorus grouping can be prepared as described in our copending application Serial No. 225,198, filed August 16, 1938.

We claim:

1. The azo compounds having the formula:

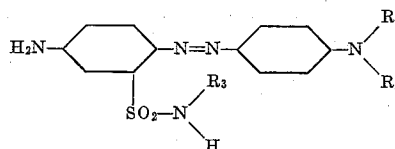


wherein R<sub>2</sub> and R<sub>3</sub> each stands for a member

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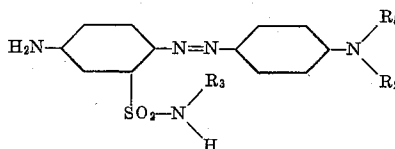
selected from the group consisting of hydrogen, a lower alkyl group, a lower alkoxyalkyl group and a lower hydroxyalkyl group, R<sub>4</sub> and R<sub>5</sub> each stands for a member selected from the group consisting of a lower alkyl group, a lower alkoxyalkyl group, a lower hydroxyalkyl group and a monocyclic group of the benzene series, X<sub>1</sub> stands for a member selected from the group consisting of hydrogen, a lower alkyl group, an acetamino group and a chlorine atom, X<sub>2</sub> stands for a member selected from the group consisting of hydrogen and a lower alkoxy group, X<sub>3</sub> stands for a member selected from the group consisting of hydrogen, a lower alkyl group, a lower alkoxy group, a chlorine atom and a bromine atom, and X<sub>4</sub> stands for a member selected from the group consisting of hydrogen and a lower alkyl group and wherein at least one of X<sub>3</sub> and X<sub>4</sub> must be hydrogen.

2. The azo compounds having the formula:



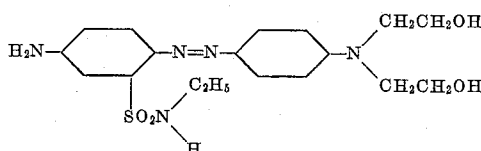
wherein R<sub>2</sub>, R<sub>3</sub> and R<sub>5</sub> each stand for a lower alkyl group.

3. The azo compounds having the formula:

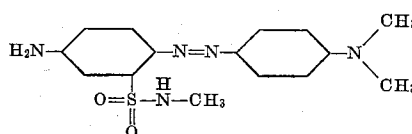


wherein R<sub>2</sub> and R<sub>5</sub> each represents a lower hydroxyalkyl group and R<sub>3</sub> represents a lower alkyl group.

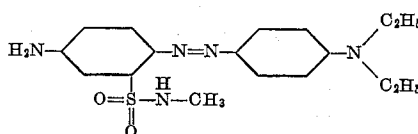
4. The azo compound having the formula:



5. The azo dye compound having the formula:



6. The azo dye compound having the formula:



JOSEPH B. DICKEY.  
JAMES G. McNALLY.