

1

2

3,438,964

HYDRAZONIUM AZO DYESTUFFS

Chi Kang Dien, Buffalo, N.Y., assignor to Allied Chemical Corporation, New York, N.Y., a corporation of New York

No Drawing, Filed Sept. 28, 1965, Ser. No. 491,042

Int. Cl. C09b 29/36, 29/00

U.S. Cl. 260—158

8 Claims

ABSTRACT OF THE DISCLOSURE

Production of 1,1-polysubstituted hydrazonium halide derivatives of 4,4'-bis(2-benzothiazolyl)azobenzene dyestuffs by reaction of a halomethyl substituted 4,4'-bis(2-benzothiazolyl)azobenzene with a polysubstituted hydrazine. The azobenzene dyestuffs of the present invention are particularly useful for dyeing cellulosic materials such as paper and cotton.

This invention relates to novel water soluble dyes and to processes for their manufacture, and more particularly it relates to novel hydrazonium dyestuffs characterized by a high degree of affinity for paper, derived from water insoluble 4,4'-bis(2-benzothiazolyl) azobenzenes.

It is known to prepare water-soluble dyestuff derivatives of water-insoluble, substituted 4,4'-bis(2-benzothiazolyl)azobenzenes by heating a halomethyl derivative of the azobenzene compound with a tertiary amine to form a quaternary ammonium salt. These known derivatives of the 4,4'-bis(2-benzothiazolyl)azobenzenes are quaternary ammonium salts useful as dyestuffs for cellulose materials such as cotton. The yellow shades obtained upon cotton are characterized by good light-fastness and decreased soap wash bleeding. However, these compounds still are limited in affinity for certain cellulose materials, such as paper.

The trend in the paper industry has been to speed up paper-making machines to such an extent that modern newsprint and tissue machines run from 2,500 to 3,000 feet a minute. When the speed of paper-making machines is thus increased, it becomes necessary to remove the water faster. At accelerated speeds, a sheet must enter the dryers with no more moisture than was present when running at slow speed. To accomplish this, suction press rolls have been added. With most dyes, this increases the loss of color on the wire side of the sheet and accentuates color two-sidedness.

There are other factors which also contribute to the problem. At the present time, most mills are using increasing amounts of so-called secondary fibers (hardwood pulps) for making paper. These pulps have more short fibers or fines than the softwood pulps, which are carried off in the white water. Unfortunately, most dyes prefer these fines to the larger fibers, so the high loss of colored fines from the wire side of the sheet leaves that

drying operation thereby resulting in a substantial color loss. The use of retention aids, or flocculating agents, to hold these materials in the sheet has met with some success but not enough to offset a relatively serious color loss.

It is, therefore, a principal object of this invention to devise new and improved water-soluble dyestuffs which readily dye cellulose materials, such as paper, yellow shades of excellent fastness to light and soaping. Another object of this invention is to devise novel water-soluble dyes which are reaction products of halomethyl-containing 4,4'-bis(2-benzothiazolyl)azobenzenes and polysubstituted hydrazines which may be easily applied to cellulose materials by direct dyeing methods.

A further object is to provide a method of preparing these novel, water-soluble, hydrazonium dyes.

Other objects will be obvious from the following description of our invention.

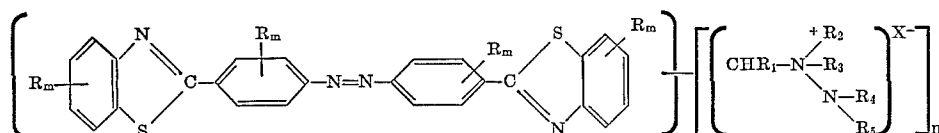
It has now been found that new hydrazonium salt type dyestuffs can be prepared which possess excellent water-solubility and affinity for cellulose materials, including paper, and which produce dyeings characterized by excellent light-fastness and little or no bleeding after soap washing. These hydrazonium salt type dyestuffs are superior in these properties especially with respect to their affinity for paper than are the above-mentioned quaternary dyestuffs prepared as for example, with triethylamine.

The new dyestuffs can be prepared by heating at least equivalent or excess portions of a halomethylated 4,4'-bis(2-benzothiazolyl)azobenzene and a 1,1-polysubstituted hydrazine in an inert organic solvent, viz. an organic solvent which does not react with either component under the reaction conditions such as, benzene, xylene and toluene. The reaction is desirably effected at temperatures of from about 50° to 100° C., and preferably from 70° to 85° C., with agitation, for about 5 to 12 hours, depending upon the degree of substitution of the dyestuff being formed.

The hydrazonium salts prepared according to the process of the present invention are new compounds in the form of solid reaction products with properties that differ from the hydrazine and halomethyl azobenzene reactants.

One property which makes the hydrazonium salts particularly useful as dyestuffs for cellulose materials is their high degree of water solubility. The salts readily dissolve in water to form yellow solutions that dye paper bright yellow shades possessing good fastness properties. The halomethyl azobenzene reactants have previously produced dyestuffs limited in water solubility and affinity for certain cellulose materials, such as paper.

The products of this invention are 1,1-poly-substituted hydrazonium halide derivatives of 4,4'-bis(2-benzothiazolyl)azobenzenes represented by the following general formula:



side lighter in color than the top side. Further, paper mills are using more loading materials such as clays, talcs and titanium in order to improve the printing qualities and opacity of the paper produced. These loadings are present in the paper composition to the extent of up to about 25 percent. Most dyes will color these fibers in preference to the pulp fibers. A substantial portion of the colored fillers are subsequently drawn off under rapid drainage and suction from the wire side of the sheet during the

wherein

n is an integer from 1 to 5;

R is hydrogen or a substituent other than a sulfonic acid or carboxylic acid group, preferably a halogen, a lower alkyl radical containing 1-6 carbon atoms inclusive or

a lower alkoxy containing 1-6 carbon atoms inclusive; m is an integer from 1 to 4;

3

R_1 is hydrogen or lower alkyl radical containing 1-6 carbon atoms inclusive;
 R_2 and R_3 are the same or different members of the group consisting of lower alkyl containing 1-6 carbon atoms inclusive; cycloalkyl, aralkyl, and aryl radicals;
 R_4 and R_5 are the same or different members of the group consisting of hydrogen and a radical represented by R_2 and R_3 ;
 X is a halogen of the group consisting of chlorine and bromine.

Suitable halomethyl derivatives of the 4,4'-bis(2-benzothiazolyl)azobenzenes for use in this invention include both the chloromethyl and bromomethyl derivatives. At least one and as many as five halomethyl groups may be attached to the 4,4'-bis(2-benzothiazolyl)azobenzene nucleus. The exact orientations of the halomethyl groups are not known but it is believed that they are attached to the terminal benzene rings of the benzothiazolyl radical rather than to the benzene rings attached to the azo linkage.

Representative members of the halomethyl derivatives of the dyestuffs of this invention include:

chloromethyl-4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene,
 di(chloromethyl-4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene,
 di(bromomethyl)-4,4'-bis(6-methyl-4-methoxy-2-benzothiazolyl)azobenzene,
 tri(bromomethyl)-4,4'-bis(6-methyl-4-chloro-2-benzothiazolyl)azobenzene,
 tetra(chloromethyl)-4,4'-bis(6-methyl-4-chloro-2-benzothiazolyl)azobenzene

In addition, it is understood that substituents may also be present in any or all of the benzene rings in the 4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene nucleus. Substituents which do not react in either the halomethyl or hydrazine reactions are suitable for this purpose and include the halogens, lower alkyl, alkoxy, and cycloalkyl radicals.

The halomethyl derivatives of the 4,4'-bis(2-benzothiazolyl)azobenzenes can be prepared by dissolving the azobenzene slowly at a temperature of from 0 to 5° C. in concentrated sulfuric acid containing a halosulfonic acid in an amount in excess of the amount required to react with the azobenzene. Then an excess of paraformaldehyde is added slowly so that no increase in temperature occurs. The solution is then heated to about 50° to 60° C. and agitated for about 3 hours. After cooling the product is recovered by filtration and washed acid-free.

Alternately, the halomethyl derivatives may be prepared by reacting a bis-halomethyl ether with the 4,4'-bis(2-benzothiazolyl)azobenzene dissolved in concentrated sulfuric acid, the reaction being conducted from about 2 to 5 hours at a temperature of from 50° to 60° C.

The number of halomethyl substituents attached to the 4,4'-bis(2-benzothiazolyl)azobenzene nucleus may be controlled by the temperature at which the reaction is conducted and by the length of the reaction period. The di- and tri-halomethylated intermediates are preferred since fewer substituents give poor solubility and more substituents tend to produce weaker dyes.

The intermediate 4,4'-bis(2-benzothiazolyl)azobenzenes are prepared by known methods, similar to the preparation of 4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene from dehydrothio-p-toluidine, as described in *Helvetica Chimica Acta* 27 1 (1944).

Suitable hydrazines for use in this invention possess

4

at least one nitrogen having two substituents other than hydrogen and may have all hydrogens replaced by alkyl, cycloalkyl, aryl, or aralkyl substituents. Specific representative examples of such hydrazines include:

5 1,1-dimethylhydrazine
 1,1-diethylhydrazine
 1-benzyl-1-methylhydrazine
 1-benzyl-1-(m-bromophenyl)hydrazine
 1-benzyl-1,2-dimethylhydrazine
 10 1-benzyl-1-(p-methoxyphenyl)hydrazine
 1-(4-biphenyl)-1-methylhydrazine
 1,1-bis(o-bromobenzyl)hydrazine
 1-(2-butoxyphenyl)-1-ethylhydrazine
 1-butyl-1-phenylhydrazine
 15 1,1-dibenzylhydrazine
 1,2-dibenzyl-1,2-dimethylhydrazine
 1,1-dibutylhydrazine
 1,1-dicyclohexylhydrazine
 1,1-diethyl-2-phenylhydrazine
 20 1,1-dipentylhydrazine
 1,2-dimethyl-1-dodecylhydrazine
 1(1-naphthyl)-1-methylhydrazine
 1,1,2-tribenzylhydrazine
 1,1,2-trimethylhydrazine

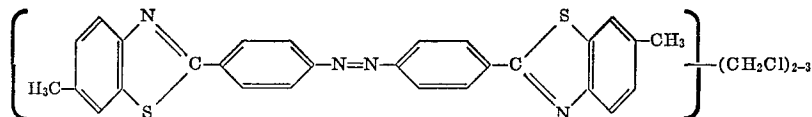
25 The substituted hydrazine is dissolved in a suitable solvent such as benzene, xylene, or toluene and added in an amount at least equimolecular to the number of halomethylated substituents on the 4,4'-bis(2-benzothiazolyl)azobenzene. The solution is agitated and heated from about 50° to 100° C. for about 5 to 12 hours. After cooling, the product is recovered by filtration and washed with benzene and dried. The yields are practically quantitative.

30 The substituted hydrazonium salts obtained by the process of this invention are dark yellow solids, very soluble in water. They are suitable for dyeing any cellulose containing material, particularly paper, to strong yellow shades with excellent wash and light-fastness, with little or no bleeding. The novel dyestuffs are suitable for blending with many similar dyes such as those disclosed in U.S. Patent No. 3,320,275 and thus can be blended to produce dyes imparting various degrees of yellow to green shadings possessing outstanding wash and light-fastness, with little or no soap wash bleeding.

45 The invention will be illustrated by the following examples. Inasmuch as variations in the details set out in these examples will be obvious to those skilled in this art and such variations can be made without departing from the scope or spirit of our invention, it is understood that the examples are for purposes of illustration only and are not intended to limit the scope of the invention.

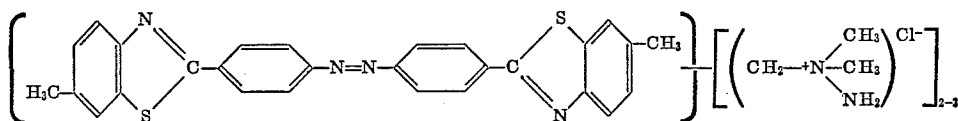
EXAMPLE I

(A) Fifty grams of 4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene were added slowly to a solution containing 67 ml. of 100% sulfuric acid and 167 ml. of chlorosulfonic acid, maintained at a temperature of 0 to 5° C. Then 67 grams of paraformaldehyde were added slowly over a period of about 30 minutes. The solution was heated to 55° C. and agitated for 3 hours. After cooling, the mixture was drawn into 3000 ml. of ice water and agitated for 18 hours. After filtration, the filter cake was washed until acid-free and dried at 70 to 80° C. A yield of 59 grams of product was obtained, having a chlorine content of 15.3% corresponding to a mixture of di- and tri-chloromethylated-4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene, having the following probable structure:



5

(B) Fifty grams of the chloromethylated derivative obtained from A above were dispersed in 300 ml. toluene, and then 35 ml. of dimethylhydrazine were added. The reaction mixture was heated to 80° C., with agitation for 6 hours. The mixture was then cooled to 25° C. and filtered. The precipitate was washed with 70 ml. of toluene and dried. A yield of 63.5 grams of product was obtained having the following probable structure:



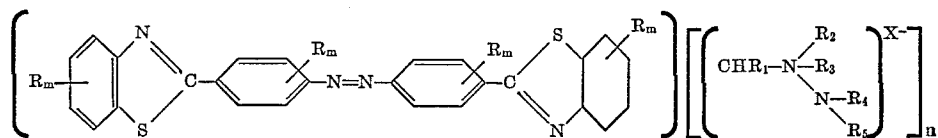
The product was very soluble in water and dyed paper with or without sizing and alum to a deep yellow shade. Light-fastness, as measured by AATCC Standard Test Method 16A-1960, at 5 and 10 s.f.h. (hours), was excellent. Soap water bleeding was negligible.

20

The product was poorly soluble in water and possessed considerably less tinctorial strength when tested for dyeing paper than the dyestuff obtained in Example I.

I claim:

1. A dyestuff having the formula:



EXAMPLE II

Example I was repeated except that the chloromethylation step was conducted at 75° to 80° C. for three hours. The product obtained in high yield contained 18.5% chlorine, corresponding very close to a tri-chloromethylated derivative.

35

The chloromethylated intermediate product thus obtained was reacted with dimethylhydrazine in the same manner as described in Example I. The product obtained was slightly weaker in dye strength than that obtained in Example I, and solubility was approximately equal. For optimum dye strength a mixture of di- and tri-chloromethylated derivatives are preferred and higher ratios of chloromethylation are not required to obtain suitable solubility.

40

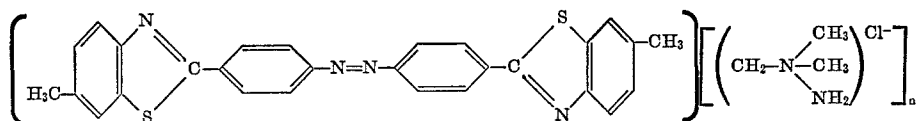
In order to more clearly demonstrate the effectiveness of the novel dyestuffs of the present invention, with respect to their affinity for paper, comparisons were made by dyeing paper with the novel dyestuffs of the present invention and the well-known cellulose dyes obtained by reacting chloromethylated 4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene and triethylamine. The tinctorial strength of the dyes on paper were evaluated according to the following scale:

50

equal
slightly less yellow
appreciably less yellow
considerably less yellow
much less yellow

60

The details of the comparative tests are set forth in the following example:



EXAMPLE III

Seven grams of the chloromethylated 4,4'-bis(6-methyl-2-benzothiazolyl)azobenzene prepared as in Example 1A

75

wherein n has a value of 2-3, the halomethyl groups of said dyestuff being attached to the terminal benzene rings of the benzothiazolyl radical.

3,438,964

7

8. A mixture of the dyestuffs of claim 7 wherein n has a value of 2 and 3.

8

CHARLES B. PARKER, *Primary Examiner*.
DONALD M. PAPUGA, *Assistant Examiner*.

References Cited

UNITED STATES PATENTS

U.S. Cl. X.R.

3,252,965 5/1966 Entschel et al. ----- 260—158

⁵ 8—7, 41, 54.2; 260—563, 569, 583