United States Patent Office

2,822,359

Patented Feb. 4, 1958

2,822,359

BENZOTHIAZOLE AZO CYCLOHEXANEDIONE-1,3 COMPOUNDS

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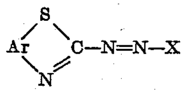
No Drawing. Application October 1, 1954
Serial No. 459,824

10 Claims. (Cl. 260—146)

This invention relates to new azo compounds and their application to the art of dyeing or coloring. More particularly it relates to metallized and non-metallized benzothiazole azo cyclohexanedione-1,3 compounds and their application to the dyeing of various textile materials. Insofar as dyeing is concerned, the invention is particularly directed to the dyeing of cellulose acetate textile materials with the metallized azo compounds of the invention.

The non-metallized monoazo compounds of our invention have the formula:

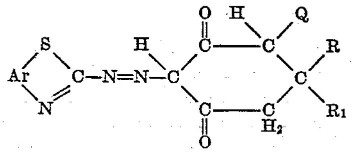
(I)



wherein Ar represents an ortho-arylene radical of the benzene series and X represents the radical of a cyclohexanedione-1,3 compound joined through the carbon atom in its 2-position to the azo bond shown. The metallized azo compounds of our invention comprise the monoazo compounds having the Formula I in complex combination with chromium, cobalt, copper, iron, manganese, nickel and vanadium. The manner of preparing the non-metallized and metallized azo compounds of our invention is fully described hereinafter.

While our invention relates broadly to the non-metallized and the metallized monoazo compounds just described, the azo compounds of our invention are represented for the most part by the non-metallized and the metallized forms of the azo compounds having the formula:

(II)

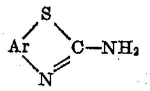


wherein Ar represents an ortho-arylene radical of the benzene series, Q represents a hydrogen atom, a methoxy group, an ethoxy group, a cyano group, a carbomethoxy group or a carboethoxy group and R and R_1 each represents a hydrogen atom, a methyl group or an ethyl group.

As is well known, one of the disadvantages dyed cellulose acetate textile fabrics suffer in comparison with some of the dyed competing textile fabrics, such as cotton, wool and viscose, for example, is lack of fastness to washing. Many schemes have been proposed to remedy this situation but all suffer from some significant fault. By means of our invention dyed cellulose acetate textile materials having good to excellent fastness to washing, light and gas are obtainable. These results may be obtained by dyeing the cellulose acetate textile material with the non-metalized dye compounds of the invention and then treating the dyed cellulose acetate textile material with suitable metal salts which cause the original dye to form metallic complexes which are resistant, for example, to the action of washing, light and gas. Thus, by means of the present invention, the disadvantage noted above with respect to the wash fastness of dyed cellulose acetate textile materials is either entirely or largely overcome.

While reference has been made to the dyeing of cellulose acetate textile materials, it is to be understood that the invention is generally applicable to the dyeing of textile materials made of or containing a cellulose alkyl carboxylic acid ester having two to four carbon atoms in the acid groups thereof. By cellulose alkyl carboxylic acid esters having two to four carbon atoms in the acid groups thereof, we mean to include, for example, both hydrolyzed and unhydrolyzed cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate-propionate and cellulose acetate-butyrate. Cellulose acetate has been particularly referred to because it is the most widely used cellulose alkyl carboxylic acid ester,

The non-metallized monoazo compounds of our invention are prepared by diazotizing a 2-aminobenzothiazole compound having the formula:



wherein Ar represents an ortho-arylene radical of the benzene series and coupling the diazonium compound obtained with a cyclohexanedione-1,3 compound.

The metallized monoazo compounds of our invention are prepared by treating the non-metallized azo compounds having the Formula I with salts of nickel, cobalt, copper, chromium, manganese, iron or vanadium. The non-metallized monoazo compounds can be metallized either on or off the fiber. Metallization can be carried out, for example, by treating the non-metallized dye with a solution or dispersion of the metallizing agent. Although the metal complex is often formed at room temperature, we prefer to accelerate the process by heating, usually with steam, for a short time. The preparation of the metallized monoazo compounds of our invention is fully described hereinafter.

Illustrative of the metallizing agents that can be employed are the halides, the sulfates, the acetates, the cyanides, and the thiocyanates of nickel, cobalt, copper, chromium, manganese, iron and vanadium. Thus, nickel chloride, nickel bromide, nickel sulfate, nickel acetate, nickel cyanide, nickel formate, nickel thiocyanate $[Ni(SCN)_2]$, cobaltous bromide, cobaltic chloride, cobaltous chloride, cobaltous acetate, cobaltous cyanide, cobalt thiocyanate $[Co(SCN)_2]$, cupric chloride, cupric bromide, cupric cyanide, cupric acetate, cupric lactate, copper thiocyanate, chromium trichloride, chromium tribromide, chromic sulfate, chromic acetate, chromium thiocyanate $[Cr(SCN)_3]$, manganese chloride, manganous sulfate, manganese acetate, manganese thiocyanate

$$[Mn(SCN)_2]$$

ferric chloride, ferric fluoride, ferrous acetate, ferrous thiocyanate $[Fe(SCN)_2]$, ferric thiocyanate $[Fe(SCN)_3]$

and vanadium thiocyanate, are illustrative of the metallizing agents that can be employed.

When the metal complex is formed on a cellulose alkyl carboxylic acid ester, such as cellulose acetate, fiber the use of a metal thiocyanate appears to be advantageous and is preferred. Nickel thiocyanate appears to be especially useful and particular claim is laid to its use. Next to nickel thiocyanate the use of cobalt thiocyanate is preferred.

2 - amino - 6 - methylsulfonylbenzothiazole, 2 - amino - 6 - ethylsulfonylbenzothiazole, 2 - amino - 6 - n - propylsulfonylbenzothiazole, 2 - amino - 6 - n - butylsulfonylbenzothiazole, 2 - aminobenzothiazole - 6 - N - methylsulfonamide, 2 - aminobenzothiazole - 6 - N - ethylsulfonamide, 2 - aminobenzothiazole - 6 - N - n - propylsulfonamide, 2 - aminobenzothiazole - 6 - N - n - butylsulfonamide, 2 - amino - 6 - methoxybenzothiazole, 2 - amino - 6 - ethoxybenzothiazole, 2 - amino - 6 - n - propoxybenzothiazole, 2 - amino - 6 - n - butoxybenzothiazole, 2 - amino - 6 - methylbenzothiazole, 2 - amino - 6 - ethylbenzothiazole, 2 - amino - 6 - n - propylbenzothiazole, 2 - amino - 6 - n - butylbenzothiazole, 2 - amino - 6 - β - hydroxyethylbenzothiazole, 2 - amino - 6 - γ - hydroxypropylbenzothiazole, 2 - amino - 6 - δ - hydroxybutylbenzothiazole, 2 - amino - 6 - acetylaminobenzothiazole, 2 - amino - 6 - n - propionylaminobenzothiazole, 2 - amino - 6 - n - butyrylaminobenzothiazole, 2 - amino - 6 - thiomethylbenzothiazole, 2 - amino - 6 - thiocyanobenzothiazole, 2 - amino - 6 - cyanobenzothiazole, 2 - amino - 6 - trifluoromethylbenzothiaozle, 2 - amino - 6 - chlorobenzothiazole, 2 - amino - 6 - nitrobenzothiazole, 2 - amino - 4,7 - dimethoxybenzothiazole, 2 - amino - 5,6 - dimethoxybenzothiazole, 2 - amino - 4,7 - diethoxybenzothiazole, and 2 - amino - 4,6 - dimethylbenzothiazole are representative of the 2-aminobenzothiazole compounds used in the preparation of the azo compounds of our invention.

Cyclohexanedione - 1,3; 5-methylcyclohexanedione-1,3; 5 - ethylcyclohexanedione - 1,3; 5,5-dimethylcyclohexanedione-1,3; 5,5-diethylcyclohexanedione-1,3; 4-carbomethoxy - 5,5 - dimethylcyclohexanedione - 1,3; 4-carboethoxy-5,5-dimethylcyclohexanedione-1,3; 4-methoxy-5,5-dimethylcyclohexanedione-1,3; 4-ethoxy - 5,5 - dimethylcyclohexanedione-1,3; 4-methyl-5,5-dimethylcyclohexanedione-1,3; 5 - phenylcyclohexanedione - 1,3; 4-phenyl-5-phenylcyclohexanedione - 1,3; 4-cyano-5-phenylcyclohexanedione-1,3; 4-cyano-6-methyl - 5 - phenylcyclohexanedione-1,3; 5-cinnamyl-6-carboethoxycyclohexanedione - 1,3; 4-cyano-5,5-dimethylcyclohexanedione - 1,3; 4-cyano-5,5-diethylcyclohexanedione-1,3; 4-methoxycyclohexanedione-1,3; 4-ethoxycyclohexanedione - 1,3; 4 - carbomethoxycyclohexanedione-1,3; 4-carboethoxycyclohexanedione-1,3; 4-methoxy-5,5-diethylcyclohexanedione - 1,3; 4-ethoxy-5,5-diethylcyclohexanedione-1,3; 4-carbomethoxy-5,5-diethylcyclohexanedione-1,3; 4-carboethoxy - 5,5 - diethylcyclohexanedione-1,3; 4-n-amylcyclohexanedione-1,3; 5-n-amylcyclohexanedione-1,3; 4,6-dibromo - 5,5 - dimethylcyclohexanedione-1,3; 5-(1-ethylpropyl)-cyclohexanedione-1,3 and 5-(p-hydroxyphenyl)-cyclohexanedione-1,3 are illustrative of the cyclohexanedione-1,3 compounds used in the preparation of the azo compounds of our invention. The use of 5,5-dimethylcyclohexanedione-1,3 appears to be advantageous.

The non-metallized monoazo dye compounds of our invention have varying utility for the dyeing of cellulose alkyl carboxylic acid esters having two to four carbon atoms in the acid groups thereof, nylon, acrylonitrile polymers, such as polyacrylonitrile and acrylonitrile graft polymers, and polyesters, such as polyethylene terephthalate. After application to these materials, usually in the form of textile materials, the dye may be metallized thereon, if desired. The metallized azo compounds of our invention can be applied by ordinary dyeing or printing techniques to nitrogenous textile materials such as wool, silk, nylon and acrylonitrile polymers, for example. Coloration can also be effected by incorporating the non-metallized or metallized azo compounds into the spinning dope, spinning the fiber as usual and converting the non-metallized azo compounds to their metallized form if desired. Also the metallizing agent can be incorporated in the spinning dope, the fiber spun as usual and then dyed with the non-metallized monoazo compounds to form the metal complex on the fiber. The new metallized dyes of our invention are preferably formed by heating the non-metallized azo dye with the metallizing agent in organic solvents, such as, for example, cellulose acetate, cellulose acetate-propionate, acrylonitrile polymers, polyamides, methyl Cellosolve and formamide.

Both the non-metallized and metallized monoazo compounds of our invention are dyes for fibers prepared from graft polymers obtained by graft polymerizing acrylonitrile alone or together with one or more other monoethylenic monomers with a preformed polymer. The preformed polymer can be a homopolymer (a polymer prepared by polymerization of a single monomer) or it can be an interpolymer such as a copolymer (a polymer prepared by the simultaneous polymerization in a single reaction mixture of two monomers) or a terpolymer (a polymer prepared by the simultaneous polymerization in a single reaction mixture of three monomers), or the like, and the graft polymers for which the dyes are particularly useful are those containing at least 5% by weight of combined acrylonitrile grafted to the preformed polymer molecule.

The graft polymers which can be dyed using the non-metallized and metallized dyes are thus polymers having directed placement of the polymerized monomeric units in the graft polymer molecule as distinguished from the random distribution obtained in interpolymers which are prepared by simultaneous polymerization of all of the monomeric materials in the polymer. The preformed polymer can be either a homopolymer of any of the well-known polymerizable monomers containing a single —CH=C< group and desirably a CH_2=C< group, or an interpolymer of two or more of such monomers; and the grafting can be effected with the preformed homopolymer or interpolymer in the polymerization mixture in which it was formed (i. e. a live polymer) or with the preformed polymer isolated from the polymerization mixture in which it was formed (i. e. a dead polymer).

The preformed polymer desirably is a homopolymer of a vinyl pyridine, an acrylamide, a maleamide, a fumaramide, an acrylate, a methacrylamide, a methacrylate, an itaconamide, a citraconamide, a fumaramate, an itaconamate, a citraconamate, a maleamate, or a vinyl ester; or an interpolymer of two or more of such monomers with each other or of at least one of such monomers with one or more different monoethylenic monomers characterized by a —CH=C< group such as styrene, acrylonitrile, substituted styrenes, vinyl or vinylidene chlorides, vinyl ethers, dialkyl maleates, alkenyl ketones, dialkyl fumarates, acrylic acid, methacrylic acid, substituted acrylonitriles, fumaronitrile, ethylene and the like.

The graft polymerization is effected by polymerizing acrylonitrile or a mixture of acrylonitrile with any other monoethylenic monomer, including any of the monomers enumerated hereinabove, with the preformed live or dead homopolymer or interpolymer whereby the acrylonitrile alone or together with another grafting monomer is combined with the preformed polymer molecule to give a graft polymer containing from 5 to 95% by weight of combined acrylonitrile.

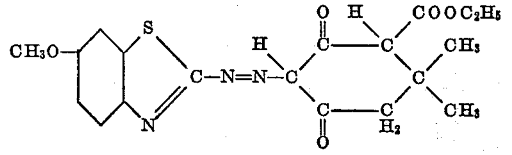
The new azo compounds of our invention are of particular utility for dyeing fibers prepared from a graft polymer obtained by graft polymerizing acrylonitrile and an acrylamide or methacrylamide with a preformed copolymer of acrylonitrile and the same or different acrylamide or methacrylamide.

U. S. Patent 2,620,324 issued December 2, 1952, U. S. Patent 2,649,434 issued August 18, 1953, and U. S. Patent 2,657,191 issued October 27, 1953, disclose other typical graft polymers that can be dyed with the new azo compounds of our invention.

The following examples in which parts are expressed as parts by weight illustrate our invention.

EXAMPLE 1

50 parts of propionic-acetic (1:5) acids were added at 10° C. to a solution of 3.8 parts of sodium nitrite in 45 parts of concentrated sulfuric acid (94%). A solution of 9.1 parts of 2-amino-6-methoxybenzothiazole in 50 parts of propionic-acetic (1:5) acids was added at 5° C. to the sodium nitrite solution and the resulting reaction mixture was stirred for 2 hours at 5° C. The diazonium solution thus obtained was added at 5° C. to a solution of 9.8 parts of 4-carboethoxy-5,5-dimethylcyclohexanedione-1,3 in 150 parts of propionic-acetic (1:5) acids. After 2 hours stirring at room temperature, the reaction mixture was made neutral to Congo red paper with ammonium acetate (sodium acetate can also be used) and then drowned in 2000 parts of cold water. The reaction product which precipitated was recovered by filtration, washed with cold water until neutral and dried at 60° C. under vacuum. 15.8 parts of the dye compound having the formula:



were obtained. This dye compound dyes cellulose acetate yellow shades.

EXAMPLE 2

130 parts of concentrated sulfuric acid were added at room temperature to a slurry of 11.4 parts of 2-amino-6-methyl-sulfonylbenzothiazole in 120 parts of water. The temperature of the reaction mixture rose to about 90° C. and the 2-amino-6-methyl-sulfonylbenzothiazole dissolved. After cooling to —10° C., a solution of 4.2 parts of sodium nitrite in 47 parts of concentrated sulfuric acid was carefully added to the reaction mixture with stirring while keeping the temperature of the reaction mixture at —5° C. or below. After stirring for 2 hours at —5° C., the diazonium solution resulting was added to a solution of 7.0 parts of 5,5-dimethylcyclohexanedione-1,3 in 150 parts of propionic-acetic (1:5) acids at 0° C. After 2 hours stirring below 5° C., the mineral acid present in the reaction mixture was made neutral to Congo red paper by the addition of sodium or ammonium acetate following which the reaction mixture was drowned in 2000 parts of cold water. The dye product which precipitated was recovered by filtration, washed well with cold water and dried at 60° C. under vacuum. 13.8 parts of a dye compound which dyes cellulose acetate yellowish-brown shades were obtained.

EXAMPLE 3

By the use of 9.75 parts of 2-amino-6-nitrobenzothiazole in Example 1 in place of 2-amino-6-methoxybenzothiazole 17 parts of a dye compound which dyes cellulose acetate yellow shades were obtained.

EXAMPLE 4

A cellulose acetate dull spun fabric dyed with a 3% dyeing of the dye product of Example 1 was padded with a 2% aqueous solution of nickel thiocyanate under conditions such that a 60 to 100% pick-up based on the weight of the fabric was obtained. The cellulose acetate fabric was air dried and then aged in a steam chest at 5 p. s. i. pressure for 20 minutes following which it was scoured at 60° C. with soap and water, rinsed well with water and dried. By this treatment the original yellow dye fabric was dyed a pleasing red shade. No bleeding was observed when a sample of the dyed fabric was subjected to a standard AATCC wash test at 160° F. with soap and water. Further, while the original yellow dyeing showed a break after 5 hours on the Fade-Ometer, the metallized dyeing showed no fading after 20 hours exposure on the Fade-Ometer.

EXAMPLE 5

A cellulose acetate fabric dyed with a 3% dyeing of the dye product of Example 2 was treated with a 2% aqueous solution of nickel thiocyanate in accordance with the procedure described in Example 4. A striking green dyeing having excellent fastness to light and washing was obtained.

EXAMPLE 6

A cellulose acetate fabric dyed with a 3% dyeing of the dye product of Example 1 was treated with a 2% aqueous solution of ferrous thiocyanate in accordance with the procedure described in Example 4. A pleasing brown dyeing having good fastness to light and washing was obtained.

EXAMPLE 7

A cellulose acetate fabric dyed with a 3% dyeing of the dye product of Example 1 was treated with a 2% aqueous solution of ferric thiocyanate in accordance with the procedure described in Example 4. A pleasing brown dyeing having good fastness to light and washing was obtained.

EXAMPLE 8

A cellulose acetate fabric dyed with a 3% dyeing of the dye product of Example 2 was treated with a 2% aqueous solution of ferrous thiocyanate in accordance with the procedure described in Example 4. A pleasing brown dyeing having good fastness to light and washing was obtained.

EXAMPLE 9

A cellulose acetate fabric dyed with a 3% dyeing of the dye product of Example 2 was treated with a 2% aqueous solution of ferric thiocyanate in accordance with the procedure described in Example 4. A pleasing brown dyeing having good fastness to light and washing was obtained.

EXAMPLE 10

A cellulose acetate dull spun fabric dyed wtih a 3% dyeing of the dye product of Example 1 was padded with a solution of 6 parts Cuprofix (a mixture of copper sulfate and a low ureaformaldehyde resin) in 200 parts of water and then dried. The dried padded cellulose acetate fabric was then cured at 160° C. for 5 minutes and then scoured at 60° C. with a solution of 1 part of Calgon (sodium hexameta-phosphate) and 1 part of Igepal CA (a polymerized ethylene oxide-alkyl phenol condensation product) in 100 parts of water, rinsed with water and dried. The cellulose acetate fabric was dyed a Bordeaux shade having good fastness to light and washing.

EXAMPLE 11

By the use of 9.8 parts of 2-amino-6-ethoxybenzothiazole and 6.47 parts of 5,5-dimethylcyclohexanedione-1,3 in Example 1 in place of 2-amino-6-methoxybenzothiazole and 4-carboethoxy-5,5-dimethylcyclohexanedione-1,3, respectively, a good yield of a dye compound which dyes cellulose acetate yellow shades was obtained.

EXAMPLE 12

2.5 grams of the dye product of Example 11 were refluxed in 50 cc. of ethylene glycol monomethyl ether with 1.5 grams of nickelous acetate crystals and 2 cc. of 28% aqueous ammonium hydroxide for 3 hours. The reaction mixture was then cooled and poured into 2000 cc. of water containing 50 grams of sodium chloride. The metallized dye product which precipitated was recovered by filtration, washed well with cold water and dried. 2.8 grams of a red pigment were thus obtained.

EXAMPLE 13

By the use of 9.9 parts of 2-amino-6-nitrobenzothiazole and 6.5 parts of 5,5-dimethylcyclohexanedione-1,3 in Example 1 in place of 2-amino-6-methoxybenzothiazole and 4-carboethoxy-5,5-dimethylcyclohexanedione-1,3, respectively, a good yield of a dye compound which dyes cellulose acetate yellow shades was obtained.

EXAMPLE 14

2.5 grams of the dye product of Example 13, 50 cc. of ethylene glycol monomethyl ether, 1.4 grams of cobaltous chloride crystals and 2 cc. of 28% aqueous ammonium hydroxide were refluxed together for 3 hours following which the reaction mixture was cooled and poured into 2000 cc. of water containing 50 grams of sodium chloride. The dye compound which precipitated was recovered by filtration, washed well with water and dried. 2.65 grams of a yellow-brown pigment were thus obtained.

EXAMPLE 15

By the use of 2.3 grams of chromium fluoride in place of cobaltous chloride in Example 14 a dark brown pigment is obtained.

EXAMPLE 16

By the use of 10.5 parts of 2-amino-4,7-dimethoxybenzothiazole and 6.47 parts of 5,5-dimethylcyclohexanedione-1,3 in Example 1 in place of 2-amino-6-methoxybenzothiazole and 4-carboethoxy-5,5-dimethylcyclohexanedione-1,3, respectively, a good yield of a dye compound which dyes cellulose acetate yellow shades was obtained.

EXAMPLE 17

A slurry of 5 grams of the dye product of Example 16 in 100 cc. of ethyl alcohol was brought to the boiling point and 10 cc. of a 20% solution of nickel thiocyanate in water was added and the resulting mixture was refluxed for 2 hours. The cooled reaction mixture was poured into 2000 cc. of water containing 50 grams of sodium chloride. The dye compound which precipitated was recovered by filtration, washed well with cold water and dried. 5.9 grams of a dark brown pigment were thus obtained.

EXAMPLE 18

To a refluxing solution of 1.8 parts of the dye product of Example 2 in 30 cc. of acetone there were added 4 parts of 28% aqueous ammonium hydroxide followed by the addition of a solution of 2 parts of nickel acetate tetrahydrate in 30 parts of acetone. The reaction mixture was refluxed with stirring for 2 hours longer and then drowned in 300 parts of water. The metallized dye compound which precipitated was recovered by filtration, washed with water and then dried under vacuum at 60° C. 1.93 parts of a metallized dye compound which, when incorporated by known means into films, filaments, etc., of cellulose acetate, imparts greenish-grey shades of good fastness properties thereto were obtained.

EXAMPLE 19

50 parts of acetic-propionic (5:1) acid were added to a solution of 3.8 parts of sodium nitrite in 46 parts of sulfuric acid (94%) at 15° C. 9.1 parts of 2-amino-6-methoxybenzothiazole were added to the reaction mixture at a temperature below 5° C., with stirring, following which 50 parts of acetic-propionic (5:1) acid were also added. The reaction mixture thus obtained was stirred 2 hours longer at 5° C. and then added to a solution of 7 parts of 5,5-dimethylcyclohexanedione-1,3 in 150 parts of acetic-propionic (5:1) acid below 5° C. The reaction mixture was made neutral to Congo red paper (i. e. the mineral acid is neutralized) by the addition of ammonium acetate and stirred for 2 hours without cooling. Following this the reaction mixture was drowned in 1200 parts of water and the dye compound which precipitated was recovered by filtration, washed well with water and dried under vacuum at 60° C. 15.8 parts of a dye compound which colors the polyacrylonitrile graft polymers described herein rich red-brown shades having good fastness to light were obtained.

EXAMPLE 20

To a refluxing solution of 1.72 parts of the dye product of Example 19 in 30 cc. of acetone there were added 4 parts of 28% aqueous ammonium hydroxide followed by the addition of a solution of 2 parts of nickel acetate tetrahydrate in 30 parts of acetone. The reaction mixture was refluxed with stirring for 2 hours longer and then drowned in 300 parts of water. The metallized dye compound which precipitated was recovered by filtration, washed with water and then dried under vacuum at 60° C. 1.78 parts of a metallized dye compound were thus obtained. When incorporated into a cellulose acetate dope solution which is then spun into yarn, red-brown filaments having good resistance to the action of light and laundering are obtained.

EXAMPLE 21

To a refluxing solution of 1.78 parts of the dye product of Example 13 in 30 cc. of acetone there were added 4 parts of 28% aqueous ammonium hydroxide followed by the addition of a solution of 2 parts of nickel acetate tetrahydrate in 30 parts of acetone. The reaction mixture was refluxed with stirring for 2 hours longer and then drowned in 300 parts of water. The metallized dye compound which precipitated was recovered by filtration, washed with water and then dried under vacuum at 60° C. 1.81 parts of a metallized dye compound which yields rich brown shades when incorporated into cellulose acetate compositions were obtained.

The dye compounds of Examples 1, 2 and 3 color the acrylonitrile graft polymer specifically described hereinafter brown, olive and brown shades, respectively.

The following tabulation further illustrates the monoazo compounds of our invention and sets forth the colors the non-metallized compounds yield on (1) cellulose acetate and (2) on an acrylonitrile graft polymer, as well as the colors obtained on cellulose acetate when the non-metallized compounds are metallized on the fiber. The preparation of the acrylonitrile graft polymer referred to in the tabulation is described immediately following the tabulation. "C. A." refers to cellulose acetate, "Original" refers to the non-metallized dyeing and "Final" refers to the metallized dyeing.

2-Aminobenzothiazole Compound	Coupling Component	Metallizing Agent	Color on CA		Color on Acrylonitrile Graft Polymer Original
			Original	Final	
6-Nitro	4-Cyano-5-phenylcyclohexanedione-1,3	$Ni(SCN)_2$	pink	brown	brown.
Do	do	$Co(SCN)_2$	do	do	
Do	do	$Fe(SCN)_3$	do	black	
Unsubstituted	5,5-Dimethylcyclohexanedione-1,3	$Ni(SCN)_2$	yellow	brown	yellow.
Do	do	$Co(SCN)_2$	do	do	
Do	do	$Cr(SCN)_3$	do	do	
6-Nitro	4-Methoxy-5,5-dimethylcyclohexanedione-1,3	$Ni(SCN)_2$	do	orange	brown.
6-Methoxy	4-Carbomethoxy-5,5-dimethylcyclohexanedione-1,3.	$Ni(SCN)_2$	do	red	red.
Do	4-Carbethoxy-5,5-dimethylcyclohexanedione-1,3	$Ni(SCN)_2$	do	do	brown.
4,7-Dimethoxy	5,5-Dimethylcyclohexanedione-1,3	$Ni(SCN)_2$	do	brown	Do.
6-Methoxy	do	$Ni(SCN)_2$	do	red	Do.
Do	do	$Co(SCN)_2$	do		
Do	do	$Fe(SCN)_3$	do	brown	
6-N-Ethylsulfamido	do	$Ni(SCN)_2$	do	grey	Do.
Do	do	$Fe(SCN)_3$	do	brown	
6-β-Hydroxyethyl	do	$Ni(SCN)_2$	do	do	Do.
Do	do	$Co(SCN)_2$	do	do	
Do	4-Ethoxy-5,5-dimethylcyclohexanedione-1,3	$Ni(SCN)_2$	do	pink	Do.
Do	do	$Co(SCN)_2$	do	grey	
Do	4-Cyano-5-phenylcyclohexanedione-1,3	$Ni(SCN)_2$	pink	red	red.
Do	do	$Co(SCN)_2$	do	grey	
6-Cyano	5,5-Dimethylcyclohexanedione-1,3	$Ni(SCN)_2$	yellow	violet	violet.
Do	do	$Co(SCN)_2$	do	grey	
6-Ethoxy	do	$Ni(SCN)_2$	do	red	orange.
Do	do	$Co(SCN)_2$	do	brown	
4-Methoxy	do	$Ni(SCN)_2$	do	do	Do.
Do	do	$Co(SCN)_2$	do	do	
6-Methylthio	do	$Ni(SCN)_2$	do	do	brown.
Do	do	$Co(SCN)_2$	do	do	
5-Methoxy	do	$Ni(SCN)_2$	do	orange	orange.
Do	do	$Co(SCN)_2$	do	brown	
5,6-Dimethoxy	do	$Ni(SCN)_2$	do	red-violet	brown.
Do	do	$Co(SCN)_2$	do	pink	
6-Nitro	do	$Ni(SCN)_2$	do	yellow	Do.
Do	do	$Co(SCN)_2$	do	do	
Do	5-Methylcyclohexanedione-1,3	$Ni(SCN)_2$	do	orange	Do.
Do	do	$Co(SCN)_2$	do	do	
Do	Cyclohexanedione-1,3	$Ni(SCN)_2$	do	do	orange.
Do	do	$Co(SCN)_2$	do	do	
6-Methoxy	do	$Ni(SCN)_2$	do	red	red.
Do	do	$Co(SCN)_2$	do	brown	
6-Methylsulfonyl	5-Methylcyclohexanedione-1,3	$Ni(SCN)_2$	do	green	green.
Do	do	$Co(SCN)_2$	do	grey	
Do	Ethyl 5,5-dimethylcyclohexanedione-1,3-carboxylate-4.	$Ni(SCN)_2$	do	orange	brown.
Do	do	$Co(SCN)_2$	do	brown	

Preparation of acrylonitrile graft polymer

3.0 g. of acrylonitrile and 7.0 g. of N-methyl methacrylamide were emulsified in 40 cc. of water containing 0.15 g. of potassium persulfate and 0.01 g. of tertiary dodecyl mercaptan. The emulsion was heated at 60° C. until 94% or more of the monomers had copolymerized. This result is usually accomplished by heating for about 12 hours. The copolymer contained approximately 30% by weight of acrylonitrile and 70% by weight of N-methyl methacrylamide. The mixture was then cooled to room temperature, 50 cc. of water added and the mixture agitated until a homogeneous solution of dope containing 10% by weight of the copolymer resulted.

30.7 g. (3.07 g. of copolymer) of the above prepared solution or dope of the copolymer were placed in a jacketed reactor provided with an agitator and heat exchanger. There were then added 10 g. of acrylonitrile, 114 cc. of water, 0.58 g. of 85% phosphoric acid, 0.1 g. of potassium persulfate, 0.17 g. of potassium metabisulfite, 0.1 g. of tertiary dodecyl mercaptan and 0.56 g. of a 30% solution in water of N-methyl methacrylamide and the mixture heated, with stirring, to 35° C. and then allowed to level off at 37°–39° C. After the heat of polymerization had been removed and when the conversion of the acrylonitrile to polymer had reached 96% or more, which is usually accomplished in a period of about 12 hours, the temperature was raised to 90° C. The mother liquor was removed by centrifuging the polymerization mixture, the polymer precipitate being reslurried twice with water and centrifuged to a 70% moisture cake. The cake was dried under vacuum at 80° C. in an agitated dryer. The over-all yield of modified polyacrylonitrile product was over 90%. After hammer-milling, the dry powder, now ready for spinning, was stored in a moisture proof container.

The acrylonitrile graft polymer prepared as above and containing about 18% by weight of N-methyl methacrylamide was soluble in N,N-dimethylformamide. Fibers spun by extruding a solution of the polymer product in N,N-dimethylformamide into a precipitating bath had a softening temperature of about 240° C., an extensibility of about 20–30 percent depending on the drafting and relaxing conditions, and showed excellent affinity for dyes.

In order that the preparation of the azo compounds of our invention may be entirely clear, the preparation of certain intermediates used in their manufacture is described hereinafter.

Preparation of 2-amino-6-methylsulfonylbenzothiazole

A solution of 200 parts of bromine in 300 parts of acetic acid was added over the course of about 1 hour to a mixture of 171 parts of p-aminophenylmethylsulfone and 202 parts of sodium thiocyanate in 1750 parts of acetic acid. The temperature was held below 35° C. during the addition and after complete addition of the bromine-acetic acid mixture, the reaction mixture was stirred for 18 hours. The reaction product was recovered on the filter by filtration, washed with acetic acid and then dispersed in 6000 parts of water. The reaction mixture thus obtained was heated to boiling and then an alkali such as caustic soda or sodium carbonate was added until the pH of the reaction mixture was about 6. The reaction mixture was then cooled, filtered and the reaction product which collected on the filter was washed well with water and dried at 120° C. 145 to 160 parts of 2-amino-6-methylsulfonylbenzothiazole were obtained as light yellow crystals melting at 226° C.–228° C.

Preparation of 2-acetylamino-6-thiocyanobenzothiazole

To a solution of 18.6 parts of aniline and 30.4 parts of ammonium thiocyanate in 300 parts of acetic acid at 15° C. 14.2 parts of chlorine were bubbled in at 15° C.–17° C. 30 minutes after addition of the chlorine 15.6 parts of sodium acetate and 30.4 parts of ammonium thiocyanate were added to the reaction mixture. While holding the temperature of the reaction mixture below 35° C., 14.2 parts of chlorine were passed in and the reaction mixture was stirred overnight at room temperature. The solid present in the reaction mixture was recovered by filtration, washed with 50 parts of acetic acid and then suspended in 600 parts of water. The mixture thus obtained was heated to boiling and filtered. 30 parts of sodium acetate were added to the filtrate and the solid which precipitated was collected at 70° C. on a filter, washed with 200 parts of cold water and dried at 100° C. 30 parts of a product melting at 187° C.–188° C. were thus obtained.

30 parts of acetic anhydride were added at 80° C. to a solution of 52.6 parts of the above product in 81 parts of acetic acid, and the temperature of the reaction mixture was held at 80° C.–90° C. for one hour. The reaction mixture was then poured into 1000 parts of cold water and the product which precipitated was recovered by filtration, washed with 500 parts of water and then dried at 60° C. 62 parts of 2-acetylamino-6-thiocyanobenzothiazole melting at 247° C.–249° C. were thus obtained.

Preparation of 2-amino-6-ethylsulfonylbenzothiazole

A solution of 26.4 parts of crystalline sodium sulfide and 24.9 parts of 2 acetylamino-6-thiocyanobenzothiazole in 150 parts of ethyl alcohol were refluxed together for 10 minutes and after cooling the reaction mixture to 20° C., 16.3 parts of ethyl iodide were added at one time and the reaction mixture resulting was refluxed for one hour. The reaction mixture was then poured into 1000 parts of water and the product which precipitated was recovered by filtration, washed well with water and dried at 60° C. 23.6 parts of 2-acetylamino-6-ethylthiobenzothiazole melting at 168° C.–169° C. were obtained. If desired, the quality of the product can be checked by hydrolyzing a little of the product with acid to 2-amino-6-ethylthiobenzothiazole melting at 137° C.–139° C.

19 parts of 30% aqueous hydrogen peroxide were added to a solution of 15.5 parts of 2-acetylamino-6-ethylthiobenzothiazole in 53 parts of acetic acid while maintaining the temperature of the reaction mixture between 80° C.–90° C. The reaction mixture was maintained at this temperature for one hour and then poured into 500 parts of cold water. The solid present in the reaction mixture was recovered by filtration and then suspended in a mixture of 800 parts of water and 100 parts of concentrated hydrochloric acid. The reaction mixture thus obtained was heated to boiling and then filtered. The filtrate was neutralized with sodium acetate, cooled to 25° C. and filtered. The product collected on the filter was washed with cold water and dried at 60° C. 8.5 parts of 2-amino-6-ethylsulfonylbenzothiazole melting at 173° C.–175° C. were thus obtained.

Preparation of 2-amino-6-isopropylsulfonylbenzothiazole

This compound was prepared in accordance with the procedure described for the preparation of 2-amino-6-ethylsulfonylbenzothiazole using 17.76 parts of isopropyl iodide in place of ethyl iodide. The melting point of the 2-acetylamino-6-isopropylthiobenzothiazole formed during the process was 174° C.–175° C. while that of the final product 2-amino-6-isopropylsulfonylbenzothiazole was 207° C.–209° C.

2-amino-6-n-propylsulfonylbenzothiazole is similarly prepared by the use of 17.76 parts of n-propyl iodide in place of isopropyl iodide in the foregoing example.

Preparation of 2-amino-6-isobutylsulfonylbenzothiazole

This compound was prepared in accordance with the procedure described for the preparation of 2-amino-6-ethylsulfonylbenzothiazole using 14.3 parts of isobutyl bromide in place of ethyl iodide. The melting point of the 2-acetylamino-6-isobutylthiobenzothiazole obtained was 167° C.–168° C. while that of the final product 2-amino-6-isobutylsulfonylbenzothiazole was 206° C.–207° C.

2-amino-6-n-butylsulfonylbenzothiazole is similarly prepared by using 14.3 parts of n-butyl bromide in place of isobutyl bromide in the foregoing example.

Preparation of 2-amino-6-trifluoromethylsulfonylbenzothiazole

75 parts of bromine in 120 parts of acetic acid were added gradually with stirring to a solution of 98 parts of p-aminophenyltrifluoromethylsulfone and 76 parts of sodium thiocyanate in 700 parts of acetic acid. The addition of the bromine was begun at room temperature and the temperature of the reaction mixture was kept below 35° C. during the addition. The temperature ordinarily rises to about 32° C. The reaction mixture resulting was stirred for 24 hours at room temperature following which it was poured into 5000 parts of cold water and the mineral acid therein neutralized by the addition of sodium acetate with good stirring. The product which formed was recovered by filtration, washed well with cold water and dried at 110° C. 33 to 70 parts of 2-amino-6-trifluoromethylsulfonylbenzothiazole melting at 206–208° C. were thus obtained.

Preparation of 2-amino-6-trifluoromethylbenzothiazole

12.5 parts of bromine in 20 parts of acetic acid were added dropwise, with stirring, to a solution of 12.4 parts of p-aminobenzotrifluoride and 12.7 parts of sodium thiocyanate in 115 parts of acetic acid while maintaining the temperature of the reaction mixture below 35° C. The reaction mixture resulting was stirred for 12 hours following which the solid present therein was removed by filtration. The filtrate was poured into 1000 parts of water and the mineral acid therein was neutralized by the addition of sodium acetate with good agitation. The product which formed was recovered by filtration, washed well with cold water and dried under vacuum at 45° C. 7.7–10.2 parts of 2-amino-6-trifluoromethylbenzothiazole melting at 115.5–116.5° C. were thus obtained.

Preparation of 2-amino-6-β-hydroxyethylbenzothiazole

255.7 grams of bromine in 400 cc. of acetic acid were added gradually over a period of 1 hour with good stirring to a solution of 219.2 grams of p-aminophenylethyl alcohol and 259.2 grams of sodium thiocyanate in 2400 cc. of acetic acid while maintaining the temperature of the reaction mixture below 15° C. The reaction mixture resulting was stirred for 2 hours at 10° C.–12° C. and the product which formed was recovered on the filter by filtration and washed with 300 cc. of acetic acid. The product filter cake thus obtained was dissolved in 1600 cc. of water at about 40° C. and the reaction mixture was made alkaline by the addition of sodium hydroxide. The reaction mixture thus obtained was heated to boiling and then cooled to 15° C. and filtered. The product obtained on the filter was washed with water until neutral and then dried at 100° C. 206 to 230 grams of 2-amino-6-β-hydroxyethylbenzothiazole were thus obtained in the form of white crystals melting at 175° C.–177° C.

Another alkali metal thiocyanate such as potassium thiocyanate, for example, can be used in place of sodium thiocyanate in the foregoing examples. Similarly, another alkaline agent, such as sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, ammonium acetate or potassium acetate, for example, can be used to neutralize the mineral acid in place of sodium acetate.

The preparation of p-aminophenyltrifluoromethylsulfone is described in British Patent 485,592.

The non-metallized monoazo dye compounds of our invention can be applied to cellulose alkyl carboxylic acid esters having 2 to 4 carbon atoms in the acid groups thereof, nylon, an acrylonitrile polymer, such as polyacrylonitrile and acrylonitrile graft polymers, and polyester, such as polyethylene terephthalate, textile materials and the metallized azo dye compounds of our invention can be applied to nitrogenous textile materials such as, for example, wool, silk, nylon and acrylonitrile polymers, such as polyacrylonitrile and acrylonitrile graft polymers, in the form of an aqueous dispersion and are ordinarily so applied.

To illustrate, the dye compound is finely ground with a dispersing agent such as sodium lignin sulfonate, Turkey red oil, soap, or an oleyl glyceryl sulfate and the resulting mixture is dispersed in water. The dye bath thus prepared is heated to a temperature approximating 45° C.–55° C. and the textile material to be dyed is immersed in the dyebath, following which the temperature is gradually raised to 80° C.–90° C. and maintained at this temperature until dyeing is complete, usually one-half to two hours. From time to time throughout the dyeing operation, the material is worked to promote even dyeing. Upon completion of the dyeing operation, the textile material is removed from the dye bath, washed with an aqueous soap solution, rinsed well with water and dried. In the case of certain of the acrylonitrile graft polymers described hereinbefore it is necessary to dye at the boil for an extended period of time. Instances may be encountered where the fiber is not satisfactorily colored by the dyeing procedure just described. In these instances special dyeing techniques, such as the use of pressure, for example, developed by the art for the coloration of materials difficult to color may be employed.

Widely varying amounts of dye can be used in the dyeing operation. The amount of dye used can be, for example, ⅓ to 3% (by weight) of that of the textile material although lesser or greater amounts of the dye can be employed.

The following example illustrates one satisfactory way in which the fibers of the acrylonitrile graft polymers can be dyed using either the non-metallized or metallized azo compounds of our invention. 16 milligrams of dye are ground with an aqueous solution of sodium lignin sulfonate until well dispersed or alternately the dye can be dissolved in 5 cc. of hot Cellosolve. The dispersion or solution, as the case may be, is then poured into 150 cc. of water to which a small amount of a surface-active agent such as Igepon T ($C_{17}H_{33}.CO.N(CH_3).C_2H_4SO_3Na$), Nekal BX (sodium alkylnaphthalenesulfonate) or Orvus (sodium lauryl sulfate-type) has been added. The dye bath is then brought to the desired temperature and 5 grams of well wet-out fibers of the graft polymer are added thereto. Dyeing is continued until the proper shade is reached. From time to time throughout the dyeing operation, the material is worked to promote even dyeing.

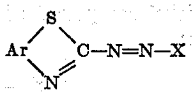
The expression "propionic-acetic (1:5) acids" refers to a mixture of propionic and acetic acids in which there are five parts by volume of acetic acid to 1 part by volume of propionic acid.

The non-metallized azo compounds dye nylon substantially the same shades as they dye acrylonitrile polymers.

Acrylonitrile graft polymers including those of the type specifically described hereinbefore are described and claimed in Coover U. S. application Serial No. 408,012, filed February 3, 1954. 2-amino-6-trifluoromethylsulfonylbenzothiazole is described and claimed by Straley and Fisher U. S. application Serial No. 413,954, filed March 3, 1954, now abandoned. 2-amino-6-trifluoromethylbenzothiazole is described and claimed by Straley and Fisher U. S. application Serial No. 413,955, filed March 3, 1954, now abandoned.

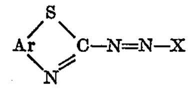
We claim:

1. A complex metal compound which contains one of the metals selected from the group consisting of chromium, cobalt, copper, iron, manganese, nickel and vanadium in complex combination with a monoazo compound having the formula:



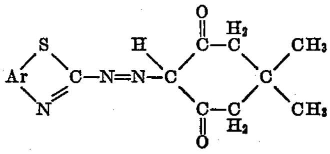
wherein Ar represents an ortho-arylene radical of the benzene series devoid of a sulfonic acid group and X represents the radical of a cyclohexanedione-1,3 compound joined through the carbon atom in its 2-position to the azo bond shown.

2. A complex metal compound which contains one of the metals selected from the group consisting of chromium, cobalt, copper, iron, manganese, nickel and vanadium in complex combination with a monoazo compound having the formula:



wherein Ar represents an ortho-arylene radical of the benzene series devoid of a sulfonic acid group and X represents the radical of a 5,5-dimethylcyclohexanedione-1,3 compound joined through the carbon atom in its 2-position to the azo bond shown.

3. A complex metal compound which contains one of the metals selected from the group consisting of chromium, cobalt, copper, iron, manganese, nickel and vanadium in complex combination with a monoazo compound having the formula:

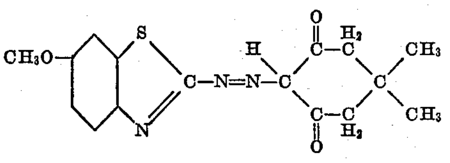


wherein Ar represents an ortho-arylene radical of the benzene series devoid of a sulfonic acid group.

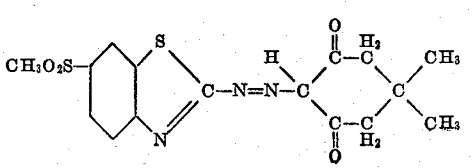
4. Complex nickel compounds of the monoazo compounds having the formula set forth in claim 1.

5. Complex cobalt compounds of the monoazo compounds having the formula set forth in claim 1.

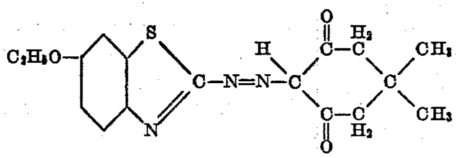
6. A complex nickel compound of the azo compound having the formula:



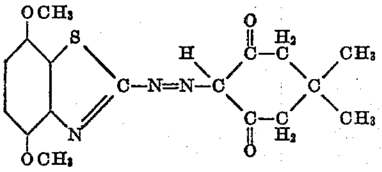
7. A complex nickel compound of the azo compound having the formula:



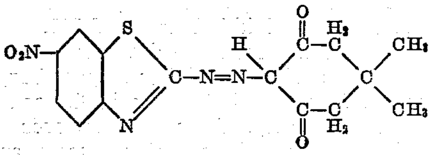
8. A complex nickel compound of the azo compound having the formula:



9. A complex nickel compound of the azo compound having the formula:



10. A complex nickel compound of the azo compound having the formula:



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