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MONAZO DYE

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4 Claims. (Cl. 260—155)

1

This invention relates to a new class of chromable monazo dyes and the process for their manufacture. More particularly it relates to a new class of chromable monazo dyes which are capable of being applied to wool by the chromate (metachrome or one-bath) method. Still more particularly this invention relates to chromable monazo dyes made by coupling selected diazos with 1,3-isoquinolinediol having various shades of red and capable of being applied to wool by the chromate method.

In the dyeing of wool with chrome dyes, modern dyers are becoming more desirous to do as much as possible of their chrome dyeing by the chromate (metachrome or one-bath) method because of the saving of valuable time and because of the fact that the final shade of the dyeing is obtained by one instead of two operations. For a dye to be applied by this method it is desirable that the chromate shade of the dye be as nearly as possible similar to the shade when applied by the after-chrome or two-bath method. It is desirable also that such a dye give a dyeing of the same strength as that obtained by the after-chrome method. The fastness properties of the chromated dye must, of course, be satisfactory since the prime purpose of using chrome dyes is that of obtaining dyeings with good light-fastness and fastness to the numerous wet treatments to which wool is subjected after the dyeing operation.

The chromate method of dyeing is a method employing a dyebath that is only faintly acid. Under these conditions of acidity the dyer may use sodium or potassium dichromate or chromate interchangeably. One of the preferred chromate methods of applying chromable dyes consists of dissolving the dye and one of the above chroming agents in the dyebath, adding ammonium acetate and the wet-out wool and gradually raising the temperature of the bath to the boiling point and maintaining this temperature for about one hour. It is believed that a good chromate dye is one capable of exhausting on the fiber evenly and completely before an appreciable amount of the dye is converted to the chromium complex. During the boiling period, however, formation of the chromium complex must be complete. It is well established that the chromate or dichromate ion in itself is incapable of forming a complex with a chromable dye. It must first be reduced to a trivalent chromium ion. This reduction may be brought about by the wool or by the dye itself. If the dye acts as the reducing agent it is nearly always partially destroyed during the process. A good chromate dye is one which is more resistant to oxidation than wool itself (see American Dyestuff Reporter Vol. 36, page 43 under "Chromation"). With all the chromable dyes from 1,3-isoquinolinediol

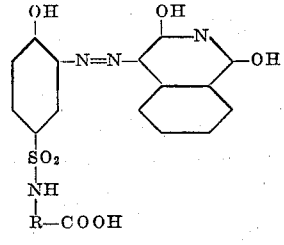
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disclosed up to the present time this has not been the case. The dyes have been destroyed almost completely in the process of reducing the chromate ions. Apparently these dyes have been more easily oxidized than the wool. Obviously the dyer would prefer to use a less expensive reducing agent since oxidation of the dye not only involves a loss of valuable material but results in unnecessary dullness in the dyeings produced.

With the manufacturer of dyes for wool facing the above requirements, it is not unexpected that during all the years of manufacturing chrome dyes few dyes have been found that satisfy all of the above requirements.

It is an object of this invention to provide novel chromable monazo dyes. A further object is to provide a chromable monazo dye which may be applied to wool by the chromate method. A further object is to produce a chromable monazo dye whose shade and strength when applied by the chromate method are similar to the shade and have the same strength as obtained when applied by the after-chrome or two-bath method. An additional object is to provide for a method of producing a chromable monazo dye capable of being chromated or after-chromed on wool with little or no resulting destruction of the dye. A further object of this invention is to provide for a chromable monazo dye whose wool dyes are characterized by good light-fastness properties and fasteness to the numerous wet treatments to which wool dyes may be subjected. Other objects will become apparent hereinafter.

I have found unexpectedly that the above objects may be accomplished by chromable dyes of the following general formula:



wherein R may be phenylene or chlorophenylene, and wherein the —COOH group is located ortho to the above shown

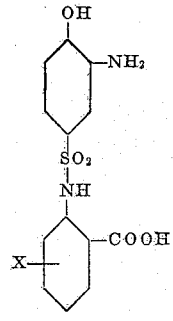


In the past it has not been possible to obtain dyes capable of being chromed on the fiber by coupling ortho-hydroxydiazo compounds to 1,3-isoquinolinediol. Meyer and Vittenet (Annales de Chemie 17, 318 (1932)) apparently failed to recognize the fact that the dye 1-amino-2-naphthol-4-sulfonic acid→1,3-isoquinolinediol prepared by them underwent very extensive oxida-

tion during the chroming stage. They report the dye itself to be red, probably as the sodium salt, and the chromed dyeing to be a brownish red. All known chromium complexes of this dye are bright violets. In attempting to repeat the work of Meyer and Vittenet, chroming of the dyed material usually resulted in a very weak tint indicating almost complete destruction of the dye. Being academic research men they probably applied the dye to wool in extremely heavy shades so that the accumulation of decomposition products appeared as a reddish brown. In industrial application this dye would be applied at the rate of 1% to 2% based on the weight of the wool and on after-chroming a very weak tint would be obtained rendering the dye as being worthless for this type of dyeing because it undergoes almost complete destruction during the after-chroming.

The German scientists found the same high degree of destruction by oxidation when they tried to after-chrome various sulfonated orthoaminophenols diazotized and coupled to 1,3-isoquinolinediol (see PB-70332, Frames 310-315, Bibliography of Scientific and Industrial Reports, Office of Technical Services, released April 30, 1948, vol. 9, No. 5).

In view of the above it was most surprising to find that an orthoaminophenol of the type:



wherein X may be hydrogen or chlorine, could be diazotized and coupled to 1,3-isoquinolinediol to give a dye capable of being chromated or after-chromed on wool with little or no destruction of the dye. Unsulfonated orthoaminophenols devoid of the sulfonanthranilide nucleus undergo extensive destruction under the same conditions. The class of dyes of this invention retain their resistance to oxidation and can be applied easily by the chromate or after-chrome method.

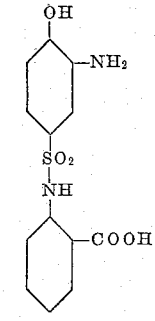
The preparation of the diazo components of this case follows known methods. Orthonitrochlorobenzene is chlorosulfonated by heating it with chlorosulfonic acid. The resulting sulfone chloride is drowned in ice and water and washed essentially free of mineral acids. It is then condensed with anthranilic acid, substituted or otherwise, in the presence of sodium bicarbonate. The condensation product is boiled several hours in caustic alkalinity to hydrolyze the chlorine ortho to the nitro group. The 2-nitrophenol-4-sulfonanilide-2'-carboxylic acid may then be reduced by any suitable method, e. g., by heating in dilute aqueous sodium sulfide, to the amino derivative.

Ordinary methods of coupling are operable. The preferred coupling medium is one having caustic alkalinity but soda ash alkalinity can be used. The diazotization is carried out preferably by the so-called inverted method. That is, the diazo component is dissolved at room temperature in sufficient water and alkali so that it is alkaline to Brilliant Yellow paper. Sodium nitrite is added to the alkaline solution and the whole is poured slowly into rapidly-agitated hydrochloric acid and ice. The resulting diazo compound is formed as a fine suspension.

Having described my invention the following examples are given to more clearly illustrate the modes of carrying the same into effect and advantageous results to be obtained thereby; all parts are by weight unless otherwise specified.

Example 1

Thirty and nine-tenths grams (30.9) of 2-amino-2'-carboxy-1-phenol - 4 - sulfonanilide of the formula:

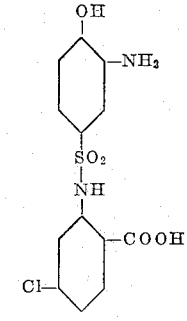


was dissolved with the aid of 8.0 grams of caustic soda in 340 grams of water at room temperature. To this solution was added 7.0 grams of sodium nitrite. This solution was added slowly with good agitation to a mixture of 13.7 grams of hydrochloric acid in 200 grams of ice. The resulting diazo compound was in the form of a fine suspension of golden yellow material. This suspension was added during about 30 minutes to a solution of 17.7 grams of isoquinolinediol and 13.6 grams of caustic soda in 400 grams of water. The coupling was very rapid. When the coupling was complete, common salt was added until the dye was precipitated. After filtration the dye was dried at 60° C.

This dye applied to wool by the chromate method dyes wool a bright bluish-red shade. The dyeings thus produced are very even and have excellent light fastness and fastness to washing and fulling.

Example 2

Seventeen and one-tenth grams (17.1) of 2-amino-2'-carboxy-5'-chloro -1- phenol-4-sulfonanilide having the formula:



was dissolved in about 500 grams of water containing four grams of caustic soda. A sodium nitrite solution corresponding to 3.5 grams of sodium nitrite was added and the combined solution poured slowly with good agitation into a solution of 6.9 grams of hydrochloric acid in 200 grams of ice and water. The resulting diazo compound was an insoluble suspension. The in-

soluble diazo compound was added slowly with good stirring to a solution of 8.9 grams of 1,3-isoquinolinediol and 6.8 grams of caustic soda in about 200 grams of water. The coupling was almost instantaneous. The coupled dye was isolated in the usual way by salting and by filtration and after being dried was applied to wool by the chromate method. The dyeing was an even red shade having good fastness properties both to light and to wet finishing treatments.

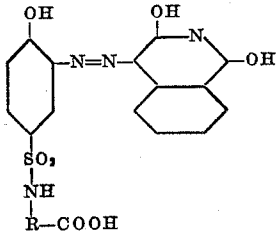
In the above Example 2, 17.1 grams of the diazo component can be replaced by 17.1 grams of the diazo components prepared from 3-chloro-2-amino-benzoic acid, 5-chloro-2-amino-benzoic acid or 6-chloro-2-amino-benzoic acid instead of the 4-chloro-2-amino-benzoic acid used in preparing the diazo component of Example 2.

The use of the resulting isomeric chloro-substituted dyes appears to have litle effect on the shade or the application properties.

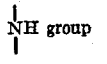
While I have disclosed the preferred embodiments of my invention, it will be apparent to those skilled in the art that many changes and variations may be made therein without departing from the spirit of my invention. Accordingly, the scope of my invention is to be limited solely by the appended claims construed as broadly as is permissible in view of the prior art.

What I claim is:

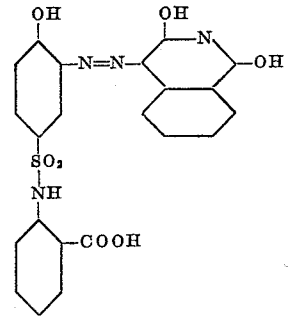
1. As a new composition of matter the chromable monazo dye having the general formula:



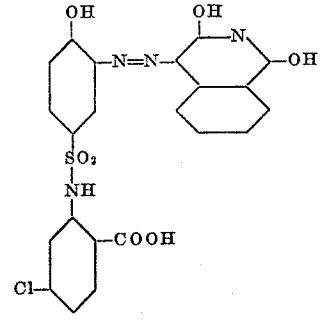
in which R is an organic radical of the group consisting of phenylene and chlorophenylene and in which the —COOH group is located ortho to the above shown



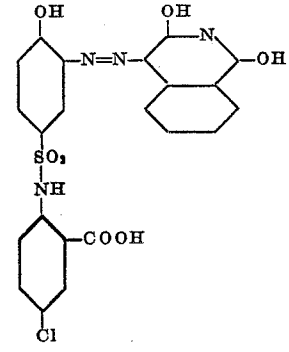
2. The chromable monazo dye of the formula:



3. The chromable monazo dye of the formula:



4. The chromable monazo dye of the formula:



BOYCE GALLOWAY CARSON.

No references cited.