AZO DYES FOR CELLULOSIC FIBERS

Ludwig Richter, Easton, Pa., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

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1. The present invention relates to azo dyes for cellulosic fibers obtained by diazotizing a 2-naphthylamine disulfonic acid, coupling the same with 5-methyl-o-anisidine, and phosgenating the resulting azo dyestuff.

Problems have been presented in providing an azo dyestuff for cotton and regenerated cellulose capable of dyeing in bright orange-yellow to orange shades and having satisfactory dischargeability and fastness to light. The problem of light fastness is particularly aggravated with respect to rayon wherein the dyed rayon is after-treated with resins to impart an antisoil finish. It has been found that even if the azo dye selected has satisfactory light fastness prior to crease-proofing, the light fastness becomes impaired by the crease-proofing operation.

It is present practice to produce variegated effects on fabrics by forming the fabrics from different fibers having varying affinities for different dyes. For instance, fabrics made from fibers composed in part of viscose rayon, and in part of acetate silk are dyed with a dyestuff of one color having affinity only for the viscose rayon and subsequently with another dyestuff of different color having affinity only for the acetate silk or viscose. The effects thus obtained are generally referred to as "estrone effects."

It has been proposed to produce urea derivatives of azo dyes derived from diazotized naphthylamine sulfo acids on the one hand and from methoxylated anilines, such as o-anisidine and 5-methyl-o-anisidine on the other hand. The prior dyestuffs, however, when used for dyeing cellulosic fibers such as cotton or regenerated cellulose, have been found to suffer in one or more of the following respects:

1. They stain estrone effects.
2. They have inferior affinity for cellulose fibers.
3. The dyes are produced in inappreciable yields.
4. The dyes yield tan or mustard shades instead of shades of orange.

Thus the urea derivatives from naphthylamine monosulfonic acids on the one hand and o-anisidine or 5-methyl-o-anisidine on the other hand stain estrone effects whereas the urea derivatives from naphthylamine trisulfonic acids and the above coupling components have inferior affinity for cellulosic fibers.

The urea derivatives from 1-naphthylamine disulfonic acids and o-anisidine are obtained in no appreciable yields. If the o-anisidine be replaced by 5-methyl-o-anisidine, either inappreciable yields of the dye are obtained or the dyes produce tan or mustard shades in lieu of a pleasant orange shade.

The urea derivatives from 2-naphthylamine disulfonic acids and o-anisidine give low yields as well as undesired shades.

It has now been discovered that urea derivatives of azo dyestuffs possessing all of the above prerequisites may be obtained by phosgenating the azo dyestuffs resulting from the diazotization of 2-naphthylamine-4,8-disulfonic acid, 2-naphthylamine-5,7-disulfonic acid, or 2-naphthylamine-6,8-disulfonic acid, and coupling the resulting diazonium compound with 5-methyl-o-anisidine. These dyes dye cotton and regenerated cellulose bright orange-yellow to orange shades distinguished by good dischargeability and an excellent light fastness. The dyes on viscose rayon with such dyes remain unimpaired as to light fastness even after the dyes have been treated to provide an anti-crease finish. The dyes leave estrone effects completely unstained.

Such dyes and their preparation constitute the purposes and objects of the present invention.

The dyes contemplated herein have the following structural formula:

\[
\text{R}=\text{N}^+ \quad \text{NH}^- \quad \text{CO} \quad \text{O}^\text{H}_2 \quad \text{O}^\text{H}_2
\]

In which R is 4,8-disulfonaphthylene, 6,8-disulfonaphthylene or 5,7-disulfonaphthylene, the naphthylene radical being linked to the azo bridge in the 2-position.

These products are prepared by diazotizing the desired 2-naphthylamine disulfonic acid and coupling it in acid solution with a molecular proportion of 5-methyl-o-anisidine. The resulting monazo dye is transformed into the urea by reacting it with phosgene at a temperature ranging from about 20 to 100 °C. in a solution with a pH from slightly acid to slightly alkaline.

The invention is further illustrated by the following examples, but it is to be understood that the invention is not restricted thereto.

**Example 1**

22 grams of 2-naphthylamine-4,8-disulfonic acid are dissolved at room temperature in 250 ml. of water to neutral reaction with about 25 ml. of sodium hydroxide solution (40% weight by volume). To this solution are added 10.5
3 ml. of hydrochloric acid (23° Bé.). This solution is run while stirring into a mixture of 250 ml. of water, ice, 5 grams of sodium nitrite and 5 ml. of hydrochloric acid (23° Bé.). 16.4 grams of 5-methyl-o-anisidine are dissolved in a solution of 60 ml. of water containing 7.4 ml. of hydrochloric acid. This solution of the coupler is run into the diazo solution while the temperature is adjusted to about 10° C. The reaction mixture is buffered to a pH of 3 to 4 with sodium acetate when coupling is finished.

Phosgene is run into the reaction mixture at a temperature between 20 and 25° C while maintaining the pH of the mixture between 7 and 8 by adding about 200 ml. of sodium hydroxide solution (40% weight by volume). The product is salted out and isolated by filtration. The weight of the dry dye is 45 grams. The dye dyes cotton and viscose rayon a bright orange, the dyes being very fast to light and having the ability to leave estro effect completely unstained.

Example II

The procedure is the same as in Example I excepting that the 2-naphthylamine-4,8-disulfonic acid is replaced by the same amount of 2-naphthylamine-5,7-disulfonic acid. After isolating and drying the product, the yield was 38.4 grams of the dye. The dyes cotton and viscose rayon an orange-yellow. The light fastness of the dye and its reaction to estro effect are similar to the dye of Example I.

Example III

The procedure is the same as in Example I excepting that the 2-naphthylamine-4,8-disulfonic acid is replaced by an identical amount of 2-naphthylamine-6,8-disulfonic acid. After isolation and drying, the yield is 37.9 grams. The material dyes cotton and viscose rayon somewhat redder than the dye of Example I.

It is to be emphasized that the utilization of the particular naphthylamine disulfonic acids is critical to the proper fulfillment of the invention. Thus, if the monoazo dye which is subsequently phosgenated is derived from 2-naphthylamine-4,8-disulfonic acid on the one hand and 5-methyl-o-anisidine on the other hand, the yield of the dye is only 32.5%. It is only when employing the particular naphthylamine-disulfonic acids noted above that all of the prerequisites of the invention are attained.

Various modifications of the invention will occur to persons skilled in this art and I therefore do not intend to be limited in the patent granted except as necessitated by the appended claims.

I claim:

1. Products of the following constitution:

   5

   \[
   \text{\begin{array}{c}
   \text{R} = \text{N=O} \\
   \text{OCH} \\
   \text{CO}_2
   \end{array}}
   \]

   wherein R is selected from the class consisting of 4,8-disulfonaphthylene, 5,7-disulfonaphthylene and 6,8-disulfonaphthylene, and in which the naphthalene ring is linked to the azo bridge in the 2-position thereof.

2. The product of the formula:

   10

   \[
   \text{\begin{array}{c}
   \text{OCH} \\
   \text{CO}_2
   \end{array}}
   \]

3. The product of the formula:

   15

   \[
   \text{\begin{array}{c}
   \text{OCH} \\
   \text{CO}_2
   \end{array}}
   \]

4. The product of the formula:

   \[
   \text{\begin{array}{c}
   \text{OCH} \\
   \text{CO}_2
   \end{array}}
   \]

   LUDWIG RICHTER.

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