252-98 CROSS REFERENCE EXAMINI

United States Patent Office 2,865,916 Patented Dec. 23, 1958

2,865,916

TRIAZOLE BRIGHTENERS

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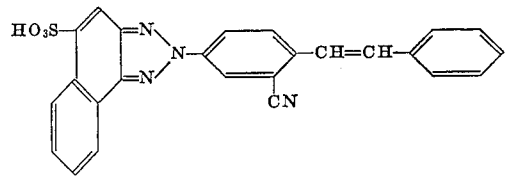
No Drawing. Application April 25, 1957 Serial No. 655,019

4 Claims. (Cl. 260—240)

This invention relates to a new brightener represented in its free acid form by the formula:



Optical bleaching agents are sometimes applied during the course of manufacture of the fabric, but most of the commercial use is found in laundering operations, either incorporated with detergent compositions or as a constituent of an acid rinsing bath, after the laundry operation with a soap or other detergent. To be useful for such a wide variety of application, there are various requirements for a good optical bleaching agent in addition to substantivity to the fiber, and a desirable shade of blue fluorescence. Thus, the compounds should be compatible with the large variety of materials encountered in soap, detergent compositions and laundry sour rinsing formulations. The solubility and dispersibility characteristics should be such that the product may be easily incorporated with the other components with which it is to be used. Application results should be consistent and show levelness of dyeing with no streaking, specking or spotting, and the strength of fluorescence should be sufficient so that only low concentrations are necessary. High stability to bleaching compositions and adequate fastness to light are also necessary.

Although many optical bleaching agents are available which have some of the necessary properties, there is still a great need for brighteners having a combination of the desirable properties listed above, while retaining high strength, desirable shade, good fabric substantivity and stability.

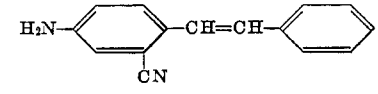
We have found that the triazole derivative described above is a superior brightener with a desirable shade of fluorescence, excellent substantivity for cellulose, nylon, and other fibers and desirable characteristics, such as high strength, ease of application, consistant dyeing results, good build-up, easy dispersibility, fastness to light and to bleaching compositions, and the like.

Various triazole derivatives of stilbene have been prepared as optical bleaching agents. Among these are 4-benzotriazolyl- and naphthotriazolyl-2-stilbene-sulfonic acids (which may carry additional sulfonic acid groups in the stilbene or arylenetriazole portions of the molecule). These compounds show certain deficiencies as brighteners. On repeated application, the build-up causes a dulling with a loss in the expected daylight whitening effect. They are also deficient in chroma, a property which is necessary for good daylight whitening. In addition, 4-naphthotriazolylstilbenes containing no sulfonic acid substituent in the stilbene portion of the molecule and lacking the cyano group as well have extremely poor fastness to light, fading out completely in five hours' exposure to sunlight.

This defect is present even in the closely similar 4-naphthotriazolyl-2-stilbene-carboxylic acid which differs only in having a carboxylic acid group in the place of the known sulfonic acid compound. Further, shifts of the position of the sulfonic acid group in the naphthalene ring seriously impairs the whitening power of the brightener. The particular structure of our invention is peculiarly advantageous. It is an advantage of the compound of our invention, that it possesses good strength with a very desirable shade of blue fluorescence. It is a further advantage that it possesses good stability to hypochlorite. It is a very important advantage of this compound that it gives good level dyeings with no specking. When applied to nylon, the compound of our invention shows a good shade of fluorescence which is more chromatic than those of the compounds of the prior art. It is a very special advantage, that when applied to nylon in repeated applications, the compound of our invention shows far better build-up with more desirable shades, with superior whitening effect, and no dulling effect. It is still further advantage and particularly surprising that when exposed to daylight, the compound of our invention has good fastness whereas, as mentioned above, the corresponding naphthotriazolylstilbenes containing no sulfonic acid group in the stilbene portion and without the cyano group of the present invention have very poor fastness. This is important for, although high fastness is not essential for many uses, the fluorescence must not be completely destroyed by several hours' exposure to sunlight, and in particular, there must be no discoloration of the cloth as a result of such an exposure. Another advantage of the compounds of our invention, is the satisfactory dispersibility and the good whitening effect on the detergent compositions in which it is incorporated.

The compound of our invention has a cyano group in the 2-position of the stilbene ring. It is most surprising to find that a compound which is substituted in this way has such superior properties. It is even more surprising to find that the position of the sulfonic acid group in the naphthalene ring is very important. It must be in the remaining alpha position of the ring to which the triazole ring is fused. Shift of this group to the other ring causes loss in the whitening power, increasing with repeated washings.

The compound of our invention is prepared by a number of methods. The most convenient method, involves diazotizing the aromatic amino derivative of the structure:



and coupling the diazo into naphthionic acid. The resulting coupling product is then converted to the triazole derivative by known methods of oxidation, such as with ammoniacal copper sulfate, sodium hypochlorite, etc.

There are a number of routes available for the preparation of amine compounds of this type, and any of these may be taken. The preferred method consists of condensing benzaldehyde with o-cyano-p-nitrotoluene or with o-cyano-p-nitrophenylacetic acid followed by reduction to the amine. Another method for the preparation of the amine involves the condensation of o-cyano-p-nitroaniline, by diazotization and coupling, with cinnamic acid in a Meerwein reaction. A third method starts with o-cyano-p-nitro- or p-aminobenzaldehyde, this being condensed with phenyl acetic acid. When the nitro compound is used, it is then reduced to the amine. In general, we find it much more preferable to use the first method described above, because the requisite aldehyde and p-nitrotoluene derivative are much more readily accessible and cheaper,

and in addition, the operations involved in the synthesis are simpler.

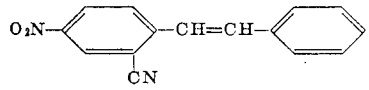
The compound of our invention is substantive to polyamides, such as nylon, to cellulose esters such as acetate rayon, and to wool. It is particularly desirable for use on cotton and nylon. For many textile uses, it is highly desirable that water solubility be a characteristic of the compound and this is obtained by the use of naphthionic acid as the coupling component, to get the compound of our invention.

Although we write it usually as the free acid, it is to be understood that we also mean the water soluble salts of the compound, such as the sodium, potassium, lithium, ammonium or amine salts, which can equally well be used.

This invention is a continuation-in-part application of our copending application Serial No. 593,810, filed June 26, 1956, now abandoned.

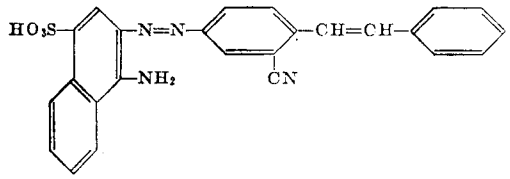
Our invention can be further illustrated by the following examples in which parts are by weight unless otherwise specified.

Example 1



A mixture of 30 parts of 2-cyano-4-nitrotoluene, 22 parts of benzaldehyde and 5 parts of piperidine is heated at 125–140° until the reaction is substantially complete. The melt is dissolved in 160 parts of hot glacial acetic acid and, on cooling, the crystalline solid which forms is filtered.

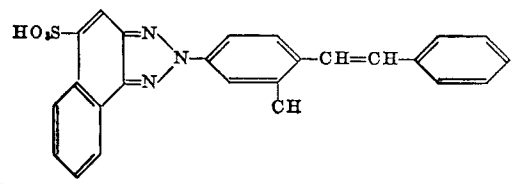
Example 2



To a boiling suspension of 9 parts of the product of Example 1 in 250 parts of 95% alcohol is added a solution of 44 parts of hydrated stannous chloride and 44 parts of concentrated hydrochloric acid. The mixture is heated at the reflux temperature until reduction is substantially complete. The mixture is then cooled and the solid is removed by filtration. It is purified by slurrying in dilute sodium hydroxide solution.

A solution of 4.4 parts of the 4-amino-2-cyanostilbene, so produced, in 120 parts of acetic acid is prepared and to it is added 8.4 parts of concentrated hydrochloric acid. Twenty-two parts of N/1 sodium nitrite solution is then added with cooling and after stirring for a short period the excess nitrite is discharged by the addition of sulfamic acid. After clarification, the diazo solution is added to a stirred solution of 6.6 parts of sodium naphthionate, 10 parts of hydrated sodium acetate and 5 parts of pyridine in 200 parts of water. After stirring for about 2 hours the mixture is acidified with concentrated hydrochloric acid and filtered. The solid is slurried in warm dilute sodium hydroxide solution and removed by filtration.

Example 3



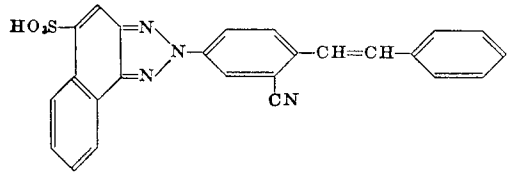
To a hot solution of the azo compound prepared in Example 2 in 560 parts of methanol, 10 parts of 5 N sodium hydroxide and 80 parts of concentrated aqueous ammonia is added a hot solution of 25 parts of hydrated copper sulfate in 100 parts of water and 80 parts of concentrated aqueous ammonia. The mixture is heated at the reflux temperature with stirring for several hours. Fifteen parts of ammonium carbonate is then added and heating is continued until triazolization is substantially complete. The mixture is cooled and the solid product is removed by filtration, slurried in aqueous ammonia and then suspended in 800 parts of methanol containing 25 parts of 5 N sodium hydroxide solution. The color of the solution is discharged by the addition of 2–3 parts of hypochlorite solution. The solid is removed by filtration. A small amount of the brightener product is obtained by concentration of the filtrate and cooling. Additional product can be extracted from the solid cake with methanol. Still additional products may be obtained by further purification of the residues and mother liquors. The crude product is further purified by recrystallization from aqueous ethanol and re-precipitation from an acid solution in methanol by the addition of sodium hydroxide solution.

Example 4

One part of the product of Example 1 is dissolved in 1000 parts of 95% alcohol and 500 parts of water at the boiling point. The volume is totaled to 2000 parts with water. Five hundred parts of the above solution is totaled to 5000 parts with water giving an 0.005% solution. Six parts of this solution is added to 19 parts of distilled water and to the resulting solution is added 100 parts of a solution of a commercial detergent (alkyl aryl sulfonate without brightener) prepared by dissolving 10 parts of the detergent in 2000 parts of water. A 5 part piece of cotton fabric is added to the prepared bath and the whole is run in a Launder-O-meter at 50° C. for 20 minutes. The cotton fabric is removed, rinsed and dried. It is much whiter and brighter in appearance than a piece of untreated cotton fabric.

We claim:

1. Compounds selected from the group consisting of the free acid of the structure:



and alkali metal ammonium and amine salts thereof.

2. The free acid of claim 1.

3. The alkali metal ammonium and amine salts of claim 1.

4. The sodium salt of claim 3.

References Cited in the file of this patent

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