BRIGHTENING AGENTS FOR POLYAMIDE FIBERS

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No Drawing. Filed Nov. 25, 1957, Ser. No. 698,386
 Claims priority, application Switzerland Nov. 30, 1956

1 Claims. (Cl. 147—33.5)

The present invention relates to the improvement of the appearance of undyed organic materials, more especially natural and synthetic polyamide fibers, and is characterized in that the said materials are treated with small quantities of colorless, blue-fluorescing compounds of the formula

\[
\begin{align*}
\text{Cl} & \quad \text{O} \\
\text{N} & \quad \text{C} \quad \text{H} \\
\text{NH} & \quad \text{NO} \\
\text{CH} & \quad \text{CH} \\
\text{NH} & \quad \text{O} \\
\text{C} & \quad \text{G} \\
\end{align*}
\]

wherein Y stands for oxygen or sulfur (O or S), R stands for a low molecular alkyl, lower alkenyl, alkoxyalkyl, or aralkyl group, and M stands for H or a cation.

It is known to brighten textile fibers by treating them with certain colloidal brightening agents or brighteners, i.e. with colorless or substantially colorless compounds which have the property, on the fiber, of fluorescing in the visible portion of the spectrum, especially in the blue-blush violet region when exposed to ultraviolet light rays. Fibers and films so treated have a brighter appearance in daylight, which contains ultraviolet rays, due to the added fluorescence.

Brighteners which are effective on polyamide fibers are of the most varying types. Thus, aminocoumarins, pyrazolines, oxycyanines, triazoles, dibenzimidazoles, etc., as well as acylation products of the diamino-stilbenesulfonic acids or reaction products of the latter with cyanuric chloride and amines, have been proposed for the brightening of polyamide fibers.

Constantly increasing requirements are currently being demanded of brightening effects, with reference to fastness to light and temperature, properties which are satisfied by present-day commercial products only to a certain extent. Particularly upon exposure to light, colored conversion products appear which seriously prejudice the brightening action.

According to the present invention, brightening effects are obtainable on polyamide fibers, especially on fibers of the type of nylon and Perlon, which effects do not become colored and are in addition temperature-stable, the said said brightening effects being obtained when the said fibers are treated with aqueous solutions of compounds of Formula I.

These compounds can be prepared e.g. by reacting in any desired order, one mole of a 4,4'-diaminostilbene-2,2'-disulfonic acid salt with two moles of a cyanuric acid halide and two moles of a compound of the formula

\[ R-Y-M' \]

wherein \( R-Y \) has the same significance as above, and \( M' \) is hydrogen or a cation, in aqueous suspension at temperatures of 0 to 20°C in first stage and of 20 to 50°C in a second stage.

Especially suitable compounds I are e.g. those wherein \( R-Y \) stands for the residue of a straight-chain or branched-chain, saturated or unsaturated or cyclic non-phenolic alcohol or ether-alcohol, which contains 1 to 7 carbon atoms in the molecule.

The compounds of this character, i.e. compounds I, are most advantageously employed in an exhausting (or drawing-on) process in quantities of 0.05 to 0.5% of the weight of the goods from neutral or weakly acid baths at temperatures between 70 and 100°C. They yield, particularly on synthetic polyamide fibers (of the type of nylon and Perlin) brightening effects of very good fastness properties, especially fastness to light, to temperature (thermo-fixing), to washing, to steaming, to perspiration, to hypochlorite and to peroxide.

The compounds I may be used alone or in combination with textile auxiliaries such as washing agents (e.g. detergents), wetting agents or softeners.

The following illustrative examples set forth presently:

**Example 1**

25 parts of undyed nylon yarn (polyamide of the adipic acid-hexamethylenediamine polycondensate type) are entered into a bath, at a temperature of 70°C, which contains 0.03% of the disodium salt of 4,4'-bis-(2-chloro-4-methoxy-1,3,5-triazyl-(6)-amino)-stilbene-2,2'-disulfonic acid and 0.3% of formic acid in 1000 parts of water. The yarn is moved around in the bath for 30 minutes at 70—80°C. The material is then rinsed with warm water and cold water, and then dried. The yarn so treated has a distinctly brighter appearance in daylight than it did prior to the treatment. The brightening effect is characterized by very good fastness properties, such as fastness to washing by hand, fastness to light and temperature stability.

A similar result is obtained if, in the present example, the disodium salt of 4,4'-bis-(2-chloro-4-methoxy-1,3,5-triazyl-(6)-amino)-stilbene-2,2'-disulfonic acid is replaced by 0.03% of the disodium salt of 4,4'-bis-(2-chloro-4-ethoxy-1,3,5-triazyl-(6)-amino)-stilbene-2,2'-disulfonic acid or of the disodium salt of 4,4'-bis-(2-chloro-4-propoxy-1,3,5-triazyl-(6)-amino)-stilbene-2,2'-disulfonic acid.

**Example 2**

30 parts of endless nylon thread (polyamide of the sebacic acid-hexamethylenediamine polycondensate type) are entered into a bath, at a temperature of 70°C, which contains 0.05% of 4,4'-bis-(2-chloro-4-ethyl-ethoxy-1,3,5-triazyl-(6)-amino)-stilbene-2,2'-disulfonic acid and 0.5% of acetic acid in 1000 parts of water.

The temperature is thereupon raised to 90°C in the course of 15 minutes and is maintained at this magnitude for 15 more minutes. The thread is then rinsed and dried. It has a brighter appearance in daylight than it had prior to the treatment.

**Example 3**

Undyed nylon-silk fabric, which has been pre-bleached with sodium chlorite, is moved about for 20 minutes at 95°C in a goods-to-liquor ratio of 1:20 in a bath which
Example 4
A bath is prepared by dissolving 0.03 part of the disodium salt of 4,4'-bis-(2-chloro-4-allyl-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid and 0.5 part of glacial acetic acid in 1000 parts of water at 80°. 25 parts of nylon gabardine are then introduced in the so-obtained bath, and the fabric moved about in the bath for 30 minutes, while raising the temperature to 90°. The material is then rinsed and dried. Viewed in daylight, the material then has distinctly brighter aspect than prior to the treatment. The brightening effect withstands, without impairment, an exposure to direct sunlight for several hours. The brightening effect is likewise of very good stability toward high temperatures (thermo-fixing), and also has very good fastness to washing, to perspiration, to steaming and to hypochlorite.

A similar effect can be obtained by using the disodium salt of 4,4'-bis-(2-chloro)-4-methallyl-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid in lieu of the disodium salt of 4,4'-bis-(2-chloro)-4-allyl-1,3,5-triazyl-(6)-(amino)-stibene-2,2'-disulfonic acid.

The nylon may be of the type used in Example 1.

Example 5
20 parts of undyed nylon underwear are washed for 30 minutes at 80° in 1000 parts of an aqueous washing bath which contains 1 part of isooctylphenyl-decaglycolether and 0.08 part of the disodium salt of 4,4'-bis-(2chloro-4-isopropoxy-1,3,5-triazyl-(6)-amino) - stibene-2,2'-disulfonic acid. The underwear, after being rinsed and dried, is distinctly brighter than a similar piece of underwear similarly washed in the absence of the said brightening agent.

A similar effect is obtained if, in the present example, the isooctylphenyl-decaglycolether is replaced by sodium dodecylbenzenesulfonate.

The nylon may be of the type mentioned in Example 1.

Example 6
On the foulard, a nylon-cretonne fabric is passed at 20° through a solution of 1 part of the disodium salt of 4,4' - bis -(2-chloro-4-n-butoxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid and 10 parts of glacial acetic acid in 1000 parts of water. The material is then squeezed down to a wet content of about 60%, the material steamed for 5 minutes at 110° and then dried at 100° C. The so-treated material is distinctly whiter, and the brightening effect possesses good stability to light.

The nylon may be of the type mentioned in Example 1.

Example 7
30 parts of undyed Perlon fabric (+-caprolactam condensate) is moved about for 30 minutes at 90-100° in a bath consisting of 1000 parts of water, 0.03 part of the tetrasodium salt of 4,4'-bis-(2-chloro-4-sec. butoxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid and 0.6 part of glacial acetic acid. After being rinsed and dried, the treated fabric shows a distinct brightening which is fast to washing and to light. A similar white enhancement is obtained when, under the same conditions, the treatment is carried out with the disodium salt of 4,4'-bis-(2-chloro-4-tert. butoxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid.

Example 8
25 parts of undyed Perlon fabric, similar to that employed in the preceding example, are treated at 90° for 30 minutes in a bath which contains, in 1000 parts of water, 0.01 part of the disodium salt of 4,4'-bis-(2-chloro-4-isobutoxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid, 0.1 part of glacial acetic acid and 0.5 part of sodium cetyl sulfate (50%). The fabric is then squeezed out to 100% wet content and dried. In daylight, the thus-treated fabric has a whiter appearance than the untreated material. A similar whitening effect is obtained if, in the foregoing, the brightener is the disodium salt of 4,4'-bis - (2 - chloro - 4 - isoamylxyloxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid.

Example 9
25 parts of chemically prebleached wool-gabardine piece goods are moved about for 30 minutes at 70-75° in a bath which contains, per 1000 parts of water, 0.5 part of the disodium salt of 4,4'-bis-(2-chloro-4-methoxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid, at a pH of 4.5 (adjusted by means of formic acid). The thus-treated wool is then rinsed and dried. In daylight, this product shows a distinct brightening of good fastness to light. This brightening effect, moreover, is stable against a 2-hour peroxide bleach at 50°.

Example 10
Natural silk is moved about for 30 minutes at 75° in a bath which contains 0.05 part of the disodium salt of 4,4'-bis-(2-chloro-4-ethoxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid and 0.2 part of acetic acid. After being rinsed and dried, the silk has a brighter aspect than prior to the treatment. A similar brightening effect is obtained if, in the same concentration, the disodium salt of 4,4'-bis-(2-chloro-4-benz oxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid or the disodium salt of 4,4'-bis-(2-chloro-p-chlorobenzoxyloxy-1,3,5-triazyl-(6)-(amino)-stibene-2,2'-disulfonic acid is used instead of the disodium salt of 4,4'-bis-(2-chloro-4-ethoxy-1,3,5-triazyl-(6)-amino)-stibene-2,2'-disulfonic acid.

The brighteners mentioned in the preceding paragraph may also be used for the brightening of polyamide fibers of the type of nylon and Perlon.

In the foregoing examples, instead of using the sodium salts, other alkali salts, such as e.g. the potassium salts, may be used with substantially the same results.

Having thus disclosed the invention, what is claimed is:
1. A process for the brightening of natural and synthetic polyamide fibers which comprises the step of treating the said fibers at a temperature above 70° C. up to about 100° C. at a pH below 7 with an aqueous solution of a compound of the formula.
wherein Y represents a member selected from the group consisting of O and S, R stands for a member selected from the group consisting of lower alkyl, lower alkoxyalkyl, and aralkyl, and M stands for a member selected from the group consisting of H and alkali metal cations.

2. A process according to claim 1, wherein the said solution contains from about 0.05 to about 0.5% by weight of thesaid compound relative to the weight of the material being treated.

3. A process according to claim 1, wherein the fibers being treated are nylon fibers.

4. A process according to claim 1, wherein the fibers being treated are Perlon fibers.

5. Polymide fibers containing thereon, as brightening agent, from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of a compound of the formula specified in claim 1, applied according to the process of claim 1.

6. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-methoxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

7. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-ethoxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

8. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-propoxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

9. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-carboxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

10. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-allyoxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

11. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-benzyloxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

12. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-methallyl-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

13. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-methylallyl-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

14. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-isoproxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

15. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-n-butoxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

16. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-n-tetrahydrofuran-3,4-sec-butoxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

17. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-carboxy-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

18. A process for the brightening of polimide fibers which comprises the step of treating the said fibers at a temperature above 70° up to about 100° C, at a pH below 7 with an aqueous solution containing from about 0.05 to about 0.5% by weight, relative to the weight of the polimide fibers, of the disodium salt of 4,4'-bis-(2-chloro-4-benzaldehyde-1,3,5-triazyl)-(6-amino)-stilbene-2,2'-disulfonic acid.

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