

# UNITED STATES PATENT OFFICE

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## METHOD OF TREATING TEXTILE MATERIALS AND THE RESULTING PRODUCTS

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This invention relates to the treatment of textile materials, such as yarns, fabrics or articles made therefrom, in order to impart thereto an apparent whiteness, and more particularly, to the treatment of white textile materials with a substantive fluorescent stilbene derivative which does not darken upon exposure to sunlight, air, or bleaching agents. It also relates to the resulting treated textiles.

It is well known that white textile materials with the lapse of time and particularly after repeated washings tend to lose their original brightness and white appearance and gradually acquire a yellow tint or similar off-white shade. To suppress or counteract this progressive deterioration in color it is customary practice in laundering operations to subject the washed material to a blueing treatment by means of a non-substantive blueing agent such as ultramarine which enhances the apparent whiteness of the materials. It is usual to give the washed material, after removal of the detergent liquid, a plurality of rinses in water and the blueing agent is generally added to the last rinse.

It has been proposed to eliminate the yellowish or off-white tint of materials such as textile fabrics, paper and the like, by treating the materials during manufacture of subsequently by immersion or otherwise with a solution of a compound of the coumarin group, preferably beta-methyl umbelliferone. While, however, beta-methyl umbelliferone and other fluorescent compounds of the coumarin group are capable of achieving a whitening effect, this effect disappears when the treated fabrics are rinsed, washed, or otherwise treated in aqueous solutions, due to the non-substantive character of the coumarin type of compounds.

It has been proposed to treat textile materials, in order to impart colored fluorescence thereto when illuminated by ultraviolet light, with relatively large amounts of a stilbene derivative, such as 4:4-dibenzoyldiaminostilbene-2:2'-disulfonic acid, which is applied to the textile in an aqueous bath containing a large amount of salt, for instance, 20% of Glauber salt. There has been no proposal of treating a textile with an aqueous solution having a very small concentration of a stilbene derivative, especially in the absence of a salt. The amount of the stilbene derivative in these particular materials which are intended to be decorative or clearly visible in ultraviolet light must be such as to impart a

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brilliant colored fluorescence when subjected to ultraviolet light in the absence of light in the visible portion of the spectrum. The color or appearance imparted to these textiles under ordinary daylight on the stilbene derivatives is not of any great concern, and there has been no proposal to use small amounts of stilbene fluorescent compounds to obtain a whitening effect in ordinary daylight without the use of a substantial amount of a salting out agent.

Another type of stilbene derivative that has been proposed as a fluorescence imparting agent is typified by 4:4'-di-p-aminobenzoyldiaminostilbene-2:2'-disulfonic acid, and other similar derivatives having a terminal  $\text{NH}_2$  group. It has been found, however, that this type of compound, when present on textile fibres, is liable to undergo undesirable changes on contact with oxidising agents, for instance, bleaching agents of the sodium hypochlorite type, as well as upon exposure to air, especially in the presence of strong sunlight, with the result that the textiles become gradually discolored. Therefore, this agent is not suitable for imparting lasting whiteness to white textile materials, especially if the treated textile is subsequently subjected to a conventional bleaching treatment.

It has been proposed to treat textiles with a stilbene derivative containing at least one triazine nucleus in the molecule in order to impart a whitened appearance to the textile. However, such materials as were obtainable from a commercial supplier showed unsatisfactory stability properties.

It has been found, and quite unexpectedly, that the above discussed disadvantages can be substantially eliminated and an improved whitening effect of greater stability and durability can be obtained by using as a treating agent a derivative of a di-aminobenzoylaminostilbene-sulfonic acid formed by the substitution of at least one of the hydrogen atoms in each of the  $\text{NH}_2$  radicals attached to the terminal rings by an organic radical which does not contain an  $\text{NH}_2$  radical directly attached to an aromatic nucleus and which would not itself render the substituted compound formed unstable to light and oxygen. The improved whitening effect and greater stability can be imparted to white textile materials, particularly cotton, linen, and other cellulosic materials.

In the laundering of white articles, sodium hypochlorite and similar bleaching agents are

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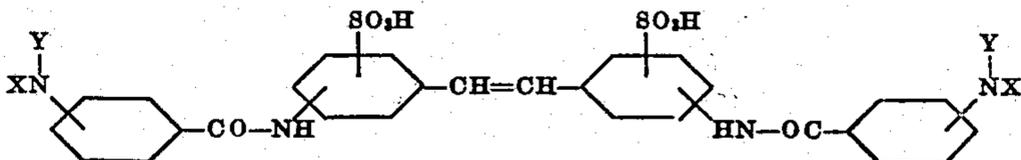
often used in the wash or in the rinse to improve the color of the material or to remove fruit, tea, coffee and similar stains. We have found that the whitening effect produced when using the specified stilbene derivatives of the invention is not impaired by such treatment, as contrasted with the detrimental effect of such treatment on stilbene derivatives used in accordance with the prior art.

The objects achieved in accordance with the

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as a benzene ring. The terminal primary amino groups of the above named compounds may be benzoylated or acetylated, etc. in the usual and well-known manner. It is essential that the aminostilbene derivative contain no primary-amino aryl groups in the molecule.

At least some of the aminostilbene derivatives which may be used in accordance with the invention may be illustrated by the following formula:



invention include the provision of a treating process for imparting an improved whitening effect of great stability to textile materials, the provision of white textile materials comprising a small proportion of an aminostilbene derivative adapted to impart an improved whitening effect of great stability thereto; and other objects which will be apparent after the invention is described in more detail hereinafter.

The stilbene derivative may be applied to white textile yarns, fibers, or fabrics before they are made up into articles of clothing, and the like, by treating the textile materials in a dilute aqueous solution of the stilbene derivative at any suitable stage in their manufacture. Alternatively, the stilbene derivative may be applied to articles of clothing, and the like, in connection with domestic or commercial laundering operations; the articles being first washed by customary methods and thereafter immersed or rinsed in a dilute aqueous solution of a stilbene derivative. In laundry practice, it is usual to give the washed product, after the removal of the detergent liquid, several rinses in clean water. The stilbene derivative may be applied in either the first or any subsequent rinse.

The accumulation of the substantive whitening agents of the invention on the textile material, such as by rinsing after repeated laundering treatments, is not harmful. It is not possible to "overblue" the textile therewith. In this respect the new agents are distinctly different than substantive blue dyes. Under the conditions of use contemplated in this disclosure, any accumulation of the aminostilbene derivatives of the invention on the textile is harmless, not only from the standpoint of appearance immediately imparted to the textile but also from the standpoint of freedom from potential darkening. The stilbene derivatives of the invention do not darken on exposure to air, sunlight, or bleaching agents, such as sodium hypochlorite. Thus, the treated textile material can be laundered repeatedly in accordance with the invention without harmful effects.

The above defined stilbene derivatives, for example, may be derived by substituting in a diaminobenzoylamino-stilbene sulfonic acid, such as 4:4'-di-p-aminobenzoylamino-stilbene-2:2'-disulfonic acid, 4:4'-di-p-aminobenzoylamino-stilbene-3:3'-disulfonic acid, 4:4'-di-p-aminobenzoylamino-stilbene-2:2',-6:6'-tetrasulfonic acid, one or both amino hydrogen atoms by an organic radical which does not itself contain a terminal NH<sub>2</sub> radical attached to an aromatic nucleus such

where X is alkyl, aryl, aroyl, acyl, or carbamyl, and Y is H, alkyl or aryl. In general, the lower aliphatic or aromatic groups are preferred as the X in the above formula. These may be typified by: methyl, ethyl, propyl, isopropyl, butyl, cyclohexyl, phenyl, methylphenyl, dimethylphenyl, benzoyl, methylbenzoyl, dimethylbenzoyl, acetyl, propionyl, butyryl and carbamyl (H<sub>2</sub>NCO—), methyl carbamyl (H<sub>3</sub>CNHCO—), ethyl carbamyl (H<sub>5</sub>C<sub>2</sub>NHCO—) and diethyl carbamyl ((H<sub>5</sub>C<sub>2</sub>)<sub>2</sub>NCO—).

The stilbene derivatives may contain one or more sulfonic acid groups and these may be attached anywhere in the molecule. The stilbene derivative may be of the symmetrical type or non-symmetrical type. The benzoyl group may be replaced by a corresponding polynuclear aroyl group. Thus, in the broader aspects of the invention, a (non-primary amino) aroylamino-stilbene sulfonic acid is used as the whitening agent. The non-primary amino groups which are directly attached to an aryl group may be secondary (i. e. R—NH—), or tertiary (i. e. R<sub>2</sub>N—), as long as R does not contain a primary amino (—NH<sub>2</sub>) group directly attached to any aryl group.

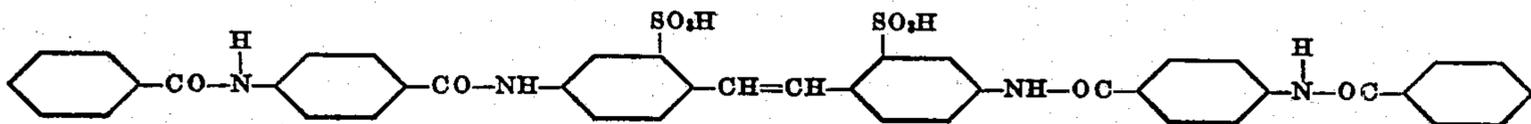
The above defined stilbene sulfonic acids may be used in the form of their salts (i. e. sodium salt) and it is intended that the term "acid" appearing herein include the acid itself and also derivatives such as the salts which contain the anion of the acid.

The aminostilbene derivative must be water soluble or dispersible in the presence of a detergent and this will exclude groups which impart thereto non-dispersibility in water.

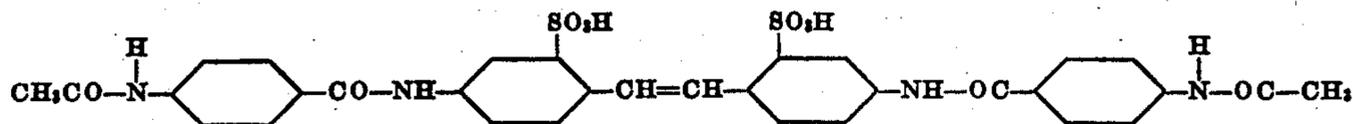
The aminostilbene derivatives used in accordance with the invention should not contain a group or radical which imparts tinctorial properties (i. e. an actual color producing or chromophorous group) or groups which tend to discolor upon exposure to light, air, or bleaching agents such as sodium hypochlorite (i. e. potential color producing or chromophorous groups). For instance, phenolic hydroxy groups would be unsuitable since such phenolic compounds are known to discolor upon exposure to air. Thiophenolic groups are also excluded since they would tend to discolor upon exposure to air. All such groups are referred to as "color producing groups."

Typical examples of specific aminostilbene derivatives which may be used in accordance with the invention are:

1. 4:4'-di-p-benzoylamino-benzoylamino-stilbene-2:2'-disulfonic acid:

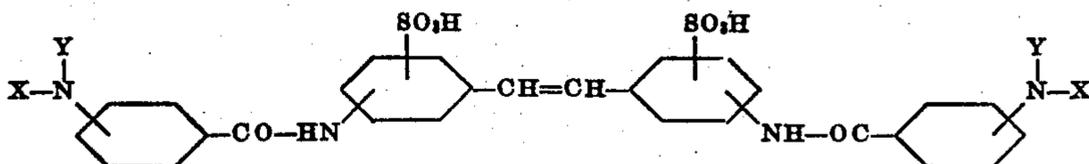


2. 4:4'-di-p - acetylamino benzoylamino - stilbene-2:2'-disulfonic acid:



as well as the corresponding meta and ortho compounds, and salts of the above acid.

The proportions in which the said stilbene derivatives are to be incorporated in the textile materials in order to achieve the objects of the invention are determined by various factors such as the particular stilbene derivative employed and the nature of the textile material to be treated. As



a general rule, considerably less than 0.05%, based on the dry weight of the textile material, is required, and proportions in the range of 0.01% to 0.0001% have been found suitable to produce the desired effect. Proportions ranging from 0.0025% to 0.0001% have been found sufficient to impart an appreciable whitened effect. The amount need not be larger than 0.05%, based on the textile material to achieve a satisfactory whitening effect.

The manner of carrying out the invention in practice and the beneficial results achieved therefrom will be apparent from the examples given below.

*Example 1*

A new white cotton cloth was rinsed for a few minutes in an aqueous bath containing 0.005% of the sodium salt of 4:4'-di-p-acetylamino benzoylamino - stilbene - 2:2' - disulfonic acid; the treated cloth after drying and ironing, showed a brilliant white appearance. The resulting treated cloth contained 0.038% of the stilbene derivative, based on the dry weight of the treated cloth. The treated cloth showed no tendency to discolor when exposed to bright sunlight over long periods, nor when stored in the dark, or treated with a dilute sodium hypochlorite solution of the strength customarily used in the bleaching of textiles.

*Example 2*

A mixed batch of towels, tablecloths, pillowcases and napkins weighing 7 pounds was washed with soap in the usual way, rinsed twice in clean water, and then given a final rinse in 7 gallons of water containing 0.005% (calculated upon the water) of the same blue-fluorescent compound as used in the above example. The resulting treated cloth articles contained 0.038% of the stilbene derivative, based on the dry weight of the treated cloth articles. The articles, when dried and ironed, were all much whiter than those in a control test laundered in the same way but without the blue-fluorescent compound, and there was no noticeable discoloration or loss of whiteness after prolonged exposure to daylight.

The foregoing descriptions of specific embodiments of the invention are for illustrative purposes only and are not to be construed as limitations of the invention as it is otherwise disclosed and claimed herein. In view of the foregoing disclosure, variations and modifications thereof will be apparent to one skilled in the art. The invention contemplates all such varia-

tions and modifications which come within the scope of the appended claims.

I claim:

1. A process which comprises applying to textile materials an amount in the range from 0.0001% to about 0.025%, based on the dry weight of the textile, of an aminoaroylamino stilbene sulfonic acid which is free from color producing groups and which has the following general formula:

in which X is a radical selected from the group consisting of aroyl and acyl radicals, and Y is a radical selected from the group consisting of hydrogen, alkyl and aryl radicals, by treatment with an aqueous solution of said acid, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

2. A process which comprises applying to textile materials an amount in the range from 0.0001% to about 0.025%, based on the dry weight of the textile, of a benzoylamino benzoylamino stilbene sulfonic acid which is free from color producing groups and primary amino groups directly attached to an aryl nucleus, by treatment with an aqueous solution of said acid, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

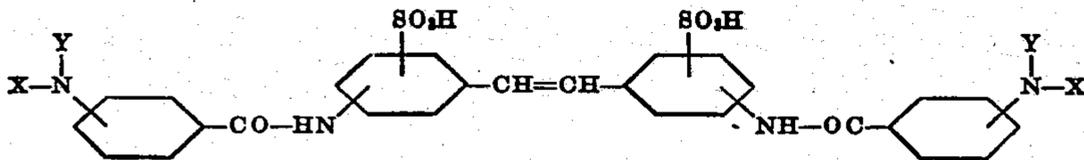
3. A process which comprises applying to textile materials an amount in the range from 0.0001% to 0.01%, based on the dry weight of the textile, of 4,4'-di-p-benzoylamino benzoylamino stilbene-2,2'-disulfonic acid which is free from color producing groups, by treatment with an aqueous solution of said acid, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

4. A process which comprises applying to textile materials an amount in the range from 0.0001% to 0.025%, based on the dry weight of the textile, of an acetylamino benzoylamino stilbene sulfonic acid which is free from color producing groups and primary amino groups directly attached to an aryl nucleus, by treatment with an aqueous solution of said acid, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

5. A process which comprises applying to textile materials an amount in the range of 0.0001% to 0.01%, based on the dry weight of the textile, of 4,4'-di-p-acetylamino benzoylamino stilbene-2,2'-disulfonic acid which is free from color producing groups by treatment with an aqueous solution of said acid, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

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6. A textile material comprising an amount in the range from about 0.0001% to about 0.025% by weight of an aminocaroylaminostilbene sulfonic acid which is free from color producing groups and which has the following general formula:



in which X is a radical selected from the group consisting of aroyl and acyl radicals, and Y is a radical selected from the group consisting of hydrogen, alkyl and aryl radicals, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

7. A textile material comprising an amount in the range from about 0.0001% to about 0.025% by weight of a benzoylaminobenzoylaminostilbene sulfonic acid free from color producing groups and primary amino groups directly attached to an aryl nucleus, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

8. A textile material comprising an amount in the range from about 0.0001% to about 0.025% by weight of an acetylaminobenzoylaminostilbene sulfonic acid free from color producing groups and primary amino groups directly attached to an aryl nucleus, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

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9. A textile material comprising an amount in the range from about 0.0001% to about 0.025% by weight of 4,4'-di-p-benzoylaminobenzoylaminostilbene-2,2'-disulfonic acid, said amount of said compound being sufficient to impart a whitening

effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

10. A textile material comprising an amount in the range from about 0.0001% to about 0.025% by weight of 4,4'-di-p-acetylaminobenzoylaminostilbene-2,2'-disulfonic acid, said amount of said compound being sufficient to impart a whitening effect to the textile material which does not discolor upon exposure to light, air and bleaching agents.

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