

## UNITED STATES PATENT OFFICE

2,624,710

COMPOSITION FOR LAUNDERING TEXTILES  
AND FOR IMPARTING A WHITENING EFFECT THEREON

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6 Claims. (Cl. 252-117)

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This invention relates to washing textiles and compositions adapted therefor. More particularly, it relates to washing white textile materials with a detergent composition comprising a substantive fluorescent stilbene derivative which does not darken upon exposure to air, sunlight, or bleaching agents, and to a detergent composition comprising such a stilbene derivative.

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 or 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. This procedure is obviously not applicable to laundering processes. 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. This type of compound is applied to the textile in an aqueous bath containing a large amount of salt, or salt plus an acid. I have observed, however, that this type of compound when present on textile fibres, is likely to undergo undesirable changes on contact with air,

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especially in the presence of strong sunlight, and also with oxidising agents, for instance, bleaching agents of the sodium hypochlorite type, 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. 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 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 by 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.

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 combination of a detergent and a blue-fluorescent compound which is a derivative of a di-aminobenzoylaminostilbene-sulfonic acid in which at least one of the hydrogen atoms in each of the NH<sub>2</sub> radicals attached to the terminal rings is substituted by an organic radical which does not contain an NH<sub>2</sub> 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 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 the



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stilbene derivatives mentioned earlier in this specification.

The objects achieved in accordance with the invention include the provision of a laundering process for washing and imparting an improved whitening effect of great stability to textile materials; the provision of laundering compositions comprising a combination of a detergent suitable for washing textile materials and a small proportion of an aminostilbene derivative adapted to impart an improved whitening effect of great stability to textile materials; and other objects which will become apparent as the invention is described in more detail hereinafter.

The process aspects of the invention comprise the step of treating textile materials to be washed in an aqueous bath containing a small proportion of an aminostilbene derivative of the kind specified, in the presence of a detergent. This is preferred since it is more convenient to incorporate the aminostilbene derivative in the detergent and the presence of the detergent does not interfere in any way with the enhanced whitening effect of the specified stilbene derivatives.

Instead of adding the specified stilbene derivatives to the wash liquor, they may be applied during the preliminary treatment of the soiled

materials which usually precedes the washing operation proper. It is a customary practice in domestic laundering to allow the soiled materials to soak for several hours, as this removes much of the soluble or loose dirt and facilitates subsequent washing. In commercial laundries a short preliminary soaking treatment is carried out by mechanically agitating the materials for a few minutes in water which is usually made slightly alkaline. This preliminary treatment is called the "break." The specified stilbene derivatives may be added to the break.

The detergent promotes cleaning of the soiled white textile materials by facilitating the removal of material adhering to the textile material. In the treating process of the invention, the whitening of the textile material with the aminostilbene derivative takes place either simultaneously with the washing-detergent action or is followed by the washing-detergent action. In either method, the textile is subjected to the effect of the combination of the detergent and the aminostilbene derivative.

It might be expected that the simultaneous or subsequent washing-detergent treatment would interfere with the absorption of the aminostilbene derivative by the textile, or that the subsequent washing-detergent treatment would remove any absorbed stilbene derivative. This is not the case, however. Instead, the presence of the detergent, along with the particular aminostilbene derivative used in accordance with the invention, results in an unexpected whitening action at the conclusion of the washing process, and this is not destroyed by rinsing or subsequent treatments.

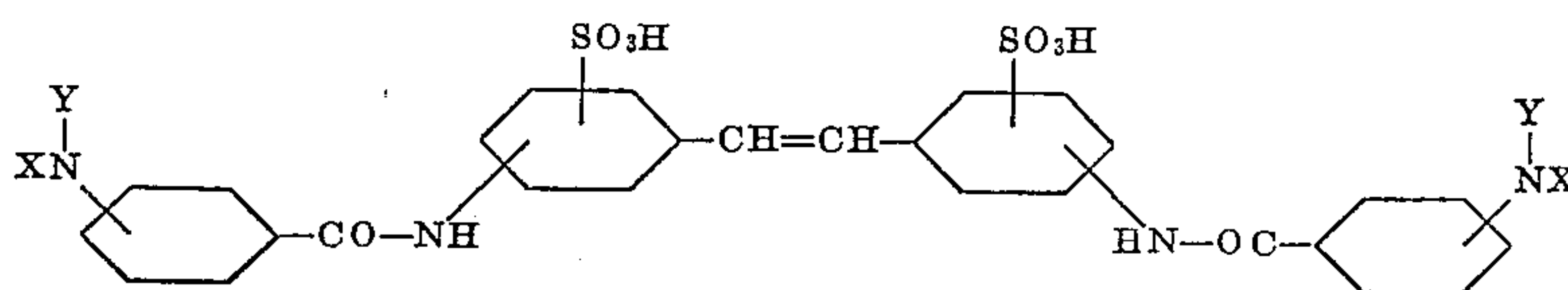
The accumulation of the substantive whitening agents of the invention on the textile material, such as by repeated laundering treatments, is not harmful. It is not possible to "over-blue" the textile therewith. In this respect the new agents are distinctly different from substantive

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blue dyes. 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  $\text{NH}_2$  radical attached to an aromatic nucleus such as a benzene ring. 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:



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 ( $\text{H}_2\text{NCO}-$ ), methyl carbamyl ( $\text{H}_3\text{CNHCO}-$ ), ethyl carbamyl ( $\text{H}_5\text{C}_2\text{NHCO}-$ ) and diethyl carbamyl ( $\text{H}_5\text{C}_2)_2\text{NCO}-$ ).

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.  $\text{R}-\text{NH}-$ ) or tertiary (i. e.  $\text{R}_2\text{N}-$ ), as long as R does not contain a primary amino ( $-\text{NH}_2$ ) 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

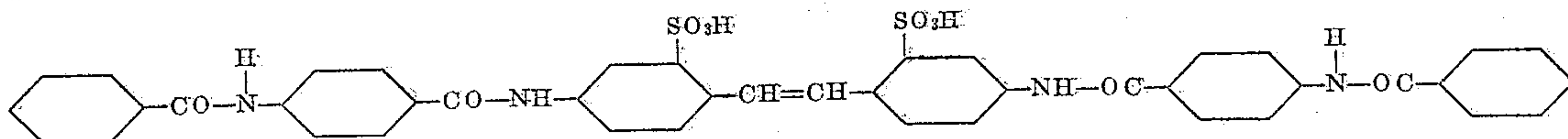


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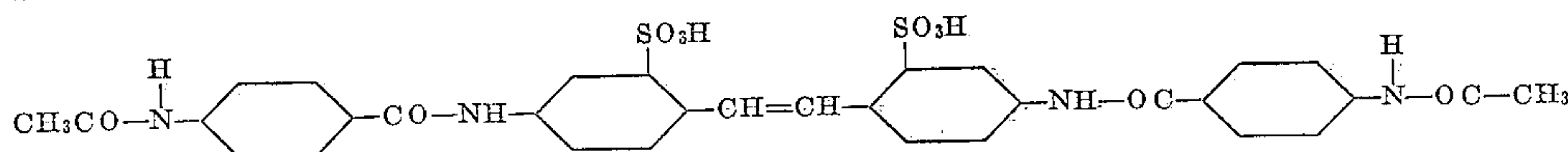
such as sodium hypochlorite (i. e. potential color producing or chromophorous groups). For instance, phenolic hydroxy groups would be unsuitable since such phenolic compounds are known to discolor upon exposure to air. Thiophenolic groups are also excluded since they would tend to discolor upon exposure 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 acids.

The detergents that are used with the stilbene compound or subsequent thereto or which are combined with the stilbene compound in a composition, are of the kind suitable for and customarily used in textile laundering practice. The suitable detergents are generally of the organic detergent type.

The organic detergents are regarded by the art as falling into the soapy and the non-soapy types. The water dispersible soapy organic detergents are salts of soap-forming carboxylic acids such as the fatty acids, rosin acids, and the like. The cation of the water dispersible soap is usually monovalent and usually an alkali metal cation such as sodium.

The non-soapy organic detergents generally are not carboxylate salts. In general, they have in the molecule a group having hydrophobic properties, such as a long chain alkyl radical, and a group having hydrophilic properties, such as a sulfonic group. The non-soapy organic detergents comprise, for example, sulfonated or sulfated high molecular fatty compounds, which are known in the art as a group of non-soapy higher fatty detergents. Some of the various compounds of this type include sodium fatty alcohol sulfates known as "Gardinols," isethionic acid, hydroxy ethyl sulfonic acid and sarcosine condensation compounds of fatty acid radicals having 8 carbon atoms or more, such as "Igepon A"; amides of various types, such as "Igepon T" and "Emco," and "Nacconols" which are alkali metal alkyl aryl sulfonates.

The expressions "soap product" and "detergent product" refer to products in a commercial marketable form comprising primarily soap or the non-soapy organic detergents, or both as the active organic detergent, in admixture with appropriate proportions of water, glycerine, filler, antioxidant, coloring matter, and other soap adjuncts present in large or small amounts as impurities or additives for special purposes. The fillers or builders which may be included in the soap product or the detergent product are typified by sodium carbonate, sodium silicate, various phosphates, and other well known soap adjuncts.

A preferred embodiment of the invention comprises a composition comprising a detergent,

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preferably ordinary laundry soap, and a small amount of the above aminostilbene derivative. The proportions of the detergent and aminostilbene derivative in the composition are determined by various factors such as the particular aminostilbene derivative employed, the nature of the textile material, the nature of the detergent, and the concentration of the detergent composition which is to be used in the aqueous dispersion or washing solution. As a general rule, less than about 1% of the aminostilbene is required, based on the weight of the detergent, and proportions ranging from about

0.001% to 0.1% have been found suitable for usual textile washing procedures.

The compositions may be in any convenient form, such as tablets or cakes of framed, milled or converted soap, flakes, and powder or granules; such as spray dried soaps, comprising the aminostilbene derivative. In general, the powder or granule form is convenient for general laundering purposes.

In the preparation of the compositions, in accordance with the invention, the aminostilbene derivative may be incorporated with the detergent at any suitable stage of manufacturing, for example, in the final stage in the soap kettle, or during the crutching or milling of soap. The aminostilbene compound may be added in the form of a solution or suspension in water, or in admixture with other ingredients, such as perfumes, antioxidants, or any other adjunct to be included in the final soap product.

The requisite amounts of aminostilbene compounds in the washing liquor or in the preliminary laundering treatment may vary within wide limits. In general, it is preferred to express this in terms of the amount of textile to be treated, and usually not over about 0.01% is necessary, based on the dry weight of the textile material to be washed. Proportions ranging from 0.0025 to 0.0001% have been found sufficient to impart an appreciable whitened effect. There is no advantage in using more than is necessary to obtain the white effect and, of course, the amounts used should be less than sufficient to impart a colored effect thereto. The amount need not be larger than 0.05%, based on the textile material to achieve a satisfactory whitening effect. However, since the use of excessive quantities of blue-fluorescent substances does not in general produce over-blueing, which is an objectionable feature of the commonly used blueing agents, higher amounts, say up to one per cent or more, may be used without detriment to the effect produced. Such higher amounts, however, usually serve no useful purpose once the quantity producing maximum whitening effect for a given case has been reached.

If the detergent composition contains 0.01 to 0.075% by weight of the aminostilbene compound and the washing liquor contains 0.25 to 0.75% of the detergent composition, the concentration in the liquor of the aminostilbene compound can be readily calculated.

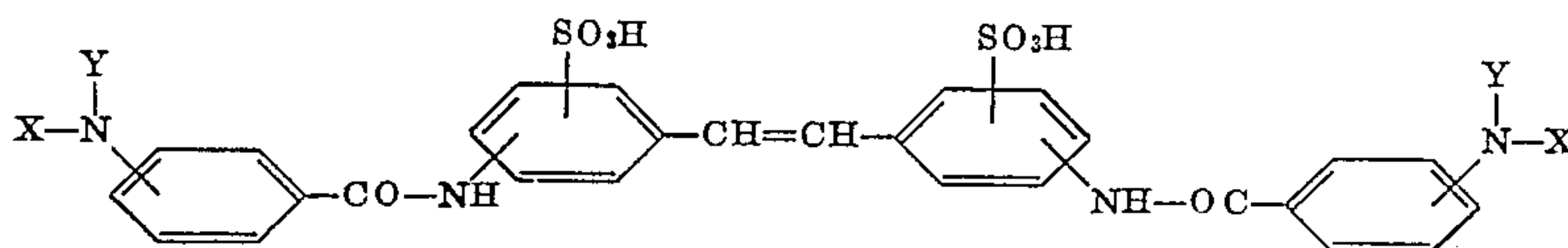


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The manner of applying the invention in practice is illustrated in the following examples. The detergent employed was ordinary laundry soap and the aminostilbene derivative was the sodium salt of 4:4'-di-p-acetylaminobenzoyl-

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tiles and for imparting a whitening effect thereto comprising a detergent suitable for laundering textiles and from about 0.001% to 1% by weight of an aminoaroylaminostilbene sulfonic acid which has the following general formula:

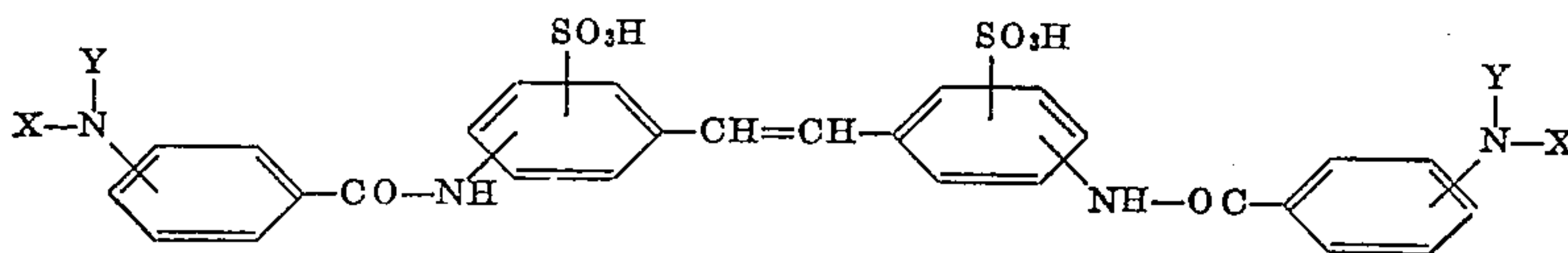


amino-stilbene-2:2'-di-sulfonic acid. Laundry compositions were made up therefrom, comprising various proportions of the aminostilbene derivative. This compound was incorporated in the soap in proportions varying from about 0.003% to 0.06% of the weight of the soap, and the resulting soap products were used for washing white cotton and linen materials in a series of comparative tests. The wash liquor was made up by dissolving about 0.4% of each soap product in hard water. The materials were washed both at about 40° C. and at the boil, rinsed three times in clean water and then dried and ironed. It was found that in every case the finished materials were of a brilliant white appearance and that the whiteness was not noticeably impaired when the materials were exposed to sunlight for prolonged periods. The higher proportions of the blue-fluorescent compound gave the best results, but even the lowest proportions showed a marked improvement. Subjecting the above washed materials to a sodium hypochlorite bleach treatment did not darken the color thereof.

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 variations and modifications as come within the scope of the appended claims.

I claim:

1. A composition suitable for laundering textiles and for imparting a whitening effect thereto comprising soap and from about 0.001% to 1% by weight of an aminoaroylaminostilbene sulfonic acid which has the following general formula:



where X is a radical selected from the group consisting of benzoyl and acetyl radicals and Y is a radical selected from the group consisting of hydrogen, alkyl radicals of not over four carbon atoms, phenyl, methylphenyl and dimethylphenyl radicals.

2. A composition suitable for laundering tex-

where 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 radicals of not over four carbon atoms, phenyl, methylphenyl and dimethylphenyl radicals.

3. A composition suitable for laundering textiles and for imparting a whitening effect thereto comprising soap and from about 0.001% to 1% by weight of a benzoylaminobenzoylaminostilbene sulfonic acid free from terminal NH<sub>2</sub> groups attached to an aryl group.

4. A laundering composition comprising soap and from about 0.001% to 1% by weight of an acetylaminobenzoylaminostilbene sulfonic acid free from terminal NH<sub>2</sub> groups attached to an aryl group.

5. A composition suitable for laundering textiles and for imparting a whitening effect thereto, comprising soap and from about 0.001% to 0.1% by weight of 4:4'-di-p-benzoylaminobenzoylaminostilbene-2:2'-disulfonic acid.

6. A composition suitable for laundering textiles and for imparting a whitening effect thereto, comprising soap and from about 0.001% to 0.1% by weight of 4:4'-di-p-acetylaminobenzoylaminostilbene-2:2'-disulfonic acid.

RICHARD THOMAS.

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