

## UNITED STATES PATENT OFFICE

2,528,324

METHOD OF TREATING PAPER AND THE  
RESULTING PRODUCTSRichard Thomas, Bromborough, England, as-  
signor to Lever Brothers Company, a corpora-  
tion of MaineNo Drawing. Application April 10, 1946, Serial  
No. 661,069. In Great Britain April 12, 1945

10 Claims. (Cl. 117—33.5)

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This invention relates to the treatment of paper in order to improve the whiteness thereof, and more particularly, to the treatment of normally white paper with a substantive fluorescent stilbene derivative which does not darken upon exposure to sunlight, air, or ink removing agents, such as hypochlorite. It also relates to the resulting treated paper.

It has been proposed to eliminate the yellowish or off-white tint of paper by treating the material by immersion or otherwise with a solution of a compound of the coumarin group, preferably beta-methyl umbelliferone. However, while the coumarin compounds are capable of achieving a whitening effect, this is not very permanent and a discoloration develops, especially upon exposure to air and sunlight. This whitening effect also may be removed when the materials are treated with hypochlorite solutions and similar ink removing agents, due to the non-substantive character of coumarin type of compounds.

It has been proposed to prepare so-called safety papers by incorporating in paper certain substantive blue-fluorescent stilbene derivatives which are non-resistant to solutions of calcium hypochlorite and similar oxidizing substances which are used as ink eradicating chemicals. Inspection of the paper under ultraviolet light will show whether such ink eradicating chemicals have been used to alter writing on the paper by the absence in the altered part of the fluorescence exhibited by the unaltered part of the paper. Non-resistant stilbene compounds must be used therein. It has been observed that such papers tend to discolor with time.

It has been found, and quite unexpectedly, that an improved whitening effect of stability and durability can be obtained by using as a treating agent a derivative of a di-aminobenzoyl-

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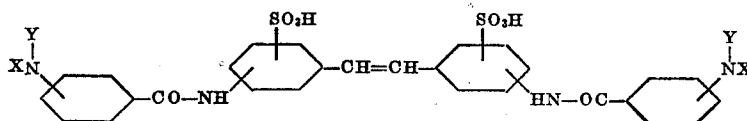
ment with a dilute solution of hypochlorite or similar ink removing agent.

The objects achieved by the present invention include the provision of a treating process for imparting an improved whitening effect of great stability to paper; the provision of paper comprising a small proportion of an aminostilbene derivative adapted to impart an improved whitening effect thereto; and other objects which will be apparent after the invention is developed in more detail hereinafter.

The stilbene derivative may be applied to normally white paper by treating the said material in a dilute aqueous solution of the stilbene derivative. If desired, the stilbene derivative may be applied to the paper after the formation into an article, such as a box or the like, or any suitable intermediate stage of the formation of the paper.

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. 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:



aminostilbene-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 stability can be imparted to paper and the like in any of several ways as described hereinafter. The resulting treated paper does not lose its improved whiteness upon treat-

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)aroylaminostilbene 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.  $R_2N-$ ), as long as R does not contain a primary amino ( $-NH_2$ ) group directly attached to any aryl group.

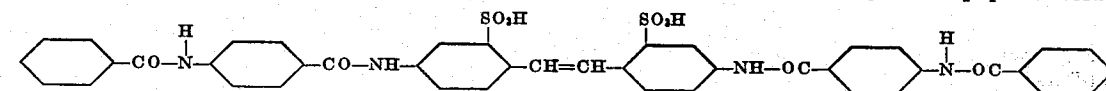
The above defined stilbene sulfonic acids may be used in the form of their salts (i. e. sodium salt) and it is intended that the term "acid compound" appearing herein include the acid itself and also derivatives such as the salts which contain the anion of the acid.

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.

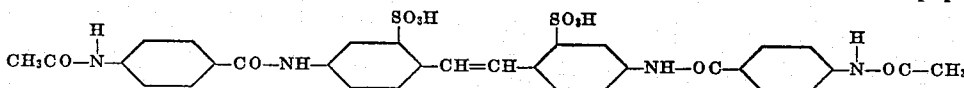
The aminostilbene derivatives used in accordance with the invention should not contain a group or radical which imparts tinctorial properties (i. e. an actual color producing or chromophorous group) or groups which tend to discolor upon exposure to light, air, or bleaching agents such as sodium hypochlorite (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 - benzoylaminobenzoylamino-stilbene-2:2'-disulfonic acid;



2. 4:4' - di - p - acetylaminobenzoylamino-stilbene-2:2'-disulfonic acid;



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

The proportions in which the said stilbene derivatives are to be incorporated in the paper 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 paper to be treated. The quantity incorporated in the paper in this way may be considerably less than 0.1% (calculated on the weight of the paper) and as little as 0.0001% has in some cases been found effective. In general, the proportions (calculated on the weight of the paper) will vary between 0.01% to 0.025% and 0.0001% but, smaller amounts can be used. In the light of the disclosure herein the optimum proportions for any given case within the ranges mentioned will be readily apparent to one skilled in the art. There is no advantage in using more than necessary to obtain the desired whitening

effect and, of course, the amounts used should be less than sufficient to impart a colored effect to the paper.

The manner of carrying out the invention in practice and the beneficial results achieved therefrom will be apparent from the following example.

#### Example 1

An 0.1% by weight solution of sodium salt of 4:4'-di - p - acetylaminobenzoylamino - stilbene-2:2'-disulfonic acid is applied to the surface of the paper at a convenient stage in its manufacture, by spraying. Alternatively, a water-dropper or any other device well known in the art for surface treatment of the paper may be used. The amount of solution applied to the paper in this way may be adjusted to leave in the paper after drying any desired percentage of the stilbene derivative in the proportions (calculated on the weight of the paper) recommended above. The resulting treated paper shows a brilliant white appearance which is not noticeably effected upon long exposure to light. The whiteness is not effected by treatment with ink eradicating agents, such as hypochlorite solutions.

If desired, the stilbene derivative may be incorporated with the cleaned and bleached pulp before its formation into paper sheet, or it may be applied to the finished paper by immersing or dipping the paper into a solution of the stilbene derivative at any stage during the manufacture of the paper or after it is manufactured.

#### Example 2

As an example of treating a paper by dipping it in a solution of a blue-fluorescent compound may be cited the following. The paper to be treated was dipped in a 0.0005% aqueous solution of 4:4'-di-p-acetylaminobenzoylamino - stilbene-2:2'-disulfonic acid. 10 parts by weight of paper were dipped in 100 parts by weight of solution for 15 minutes at 40° C., during which time the liquid was agitated continuously. The paper absorbed

an amount of the compound corresponding to 0.0036% of the weight of the paper. The paper

showed the same white appearance and had the same properties as the same prepared in accordance with Example 1. If desired a shorter time of dipping may be employed, resulting in a correspondingly smaller amount of the compound absorbed. This may be compensated for by increasing the strength of the solution.

The invention is applicable to all types of normally white paper and by the word "paper" is meant the usual broad generic definition, namely cellulosic fibrous material felted or otherwise molded into sheet or other form of varying thicknesses, including cardboard and composite sheets. In general, the paper is more or less non-transparent in visible light.

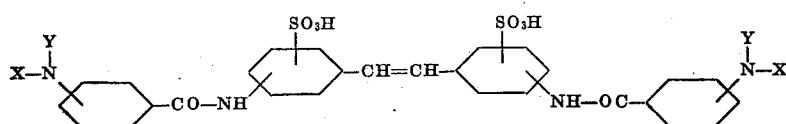
The foregoing descriptions of specific embodiments of the invention are for illustrative purposes only and are not to be construed as limitations of the invention as it is otherwise disclosed and claimed herein. In view of the foregoing

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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 process which comprises applying to paper an amount in the range from 0.0001% to about 0.025%, based on the dry weight of the paper, of an aminoaroylaminostilbene 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 paper which does not discolor upon exposure to light, air and bleaching agents.

2. A process which comprises applying to paper an amount in the range from 0.0001% to about 0.025%, based on the dry weight of the paper, of a benzoylaminobenzoylaminostilbene 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 paper which does not discolor upon exposure to light, air and bleaching agents.

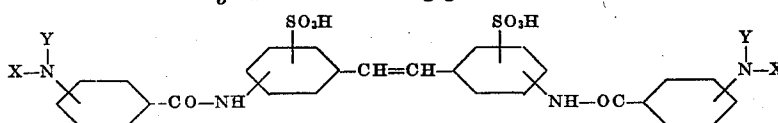
3. A process which comprises applying to paper an amount in the range from 0.0001% to 0.01%, based on the dry weight of the paper, of a 4,4'-di-p-benzoylaminobenzoylaminostilbene-2,2'-disulfonic acid which is free from color producing groups, by treatment with an aqueous solution of said acid, said amount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

4. A process which comprises applying to paper an amount in the range from 0.0001% to 0.025%, based on the dry weight of the paper, of an acetylaminobenzoylaminostilbene 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 paper which does not discolor upon exposure to light, air and bleaching agents.

5. A process which comprises applying to paper an amount in the range from 0.0001% to 0.01%, based on the dry weight of the paper, of a 4,4'-di-p-acetylaminobenzoylaminostilbene-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 paper which does not discolor upon exposure to light, air and bleaching agents.

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6. A paper comprising an amount in the range from about 0.0001% to about 0.025% by weight of an aminoaroylaminostilbene 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 paper which does not discolor upon exposure to light, air and bleaching agents.

7. A paper comprising an amount in the range from about 0.0001% to about 0.025% by weight of a benzoylaminobenzoylaminostilbene 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 paper which does not discolor upon exposure to light, air and bleaching agents.

8. A paper comprising an amount in the range from about 0.0001% to about 0.025% by weight of an acetylaminobenzoylaminostilbene 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 paper which does not discolor upon exposure to light, air and bleaching agents.

9. A paper comprising an amount in the range from about 0.0001% to about 0.01% by weight of a 4,4'-di-p-benzoylaminobenzoylaminostilbene-2,2'-disulfonic acid, said amount of said compound being sufficient to impart a whitening effect to the paper which does not discolor upon exposure to light, air and bleaching agents.

10. A paper comprising an amount in the range from about 0.0001% to about 0.01% by weight of a 4,4'-di-p-acetylaminobenzoylaminostilbene-2,2'-disulfonic acid, said amount of said compound being sufficient to impart a whitening effect to the paper which does not discolor upon exposure to light, air and bleaching agents.

RICHARD THOMAS.

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