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3,475,190

## OPTICAL BRIGHTENING OF PAPER

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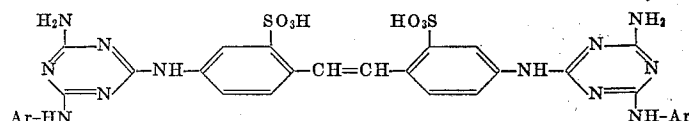
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7 Claims

### ABSTRACT OF THE DISCLOSURE

Paper is optically brightened by coating the surface of the paper with an amount to effectively optically brighten said paper of a liquor containing a compound of the formula:

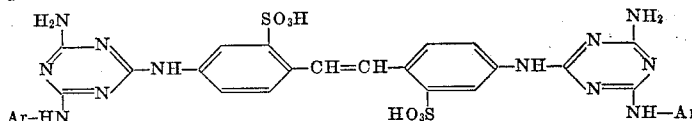


wherein Ar represents an unsubstituted phenyl radical or one containing non-coloring substituents; and water soluble salts of such compound. In the preferred embodiment, the phenyl radical is unsubstituted.

The present invention concerns the use of certain bis-s-triazinylamino-stilbene-2,2'-disulphonic acids for the optical brightening of paper, particularly by the surface coating process, the liquor usable for this purpose as well as, an industrial product, the paper having a content of these bis-s-triazinylamino-stilbene-2,2'-disulphonic acids.

In order to meet present day requirements, white un-sized and, apticularly, sized paper needs optical brightening. This whitening can be performed by treatment of the pulp with substantive optical brighteners; advantageously however, for the brightening of paper, the so-called surface coating process is used, as this process enables the optical brightening and the surface finishing to be performed simultaneously. However, the usual brighteners used for the surface coating process do not always meet the increased whitening requirements because, generally, they are not sufficiently active and, in high dosages, give the paper an undesirable greenish tinge.

It has now been found that bis-s-triazinylamino-stilbene-2,2'-disulphonic acids of general Formula I, particularly in the form of their soluble salts, are well suited for the optical brightening of paper including cardboard, in particular in the surface coating process.



In this formula, Ar represents the unsubstituted phenyl radical or one containing non-colouring substituents. Examples of non-colouring substituents are the sulphonic acid or carboxylic acid group, halogens such as fluorine, chlorine or bromine, low alkyl or alkoxy groups which contain, e.g. 1 to 5 carbon atoms. Preferably, Ar is the phenyl radical.

In particular the alkali, alkaline earth or ammonium salts, e.g. those derived from ammonia or an alkanolamine, are used as soluble salts. The disodium salt is preferred.

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Compounds of Formula I which can be used according to the invention have been described in French Patent No. 905,534 as textile brighteners.

Both unsized paper, particularly however, sized printing, writing and photographic paper, as well as cardboard can be brightened by the use of brighteners of Formula I. Both the pulp and also the paper surface can be brightened according to the invention; preferably the paper is optically brightened by the surface coating process.

In practice, the surface finishing of paper is performed by the following two methods:

- (A) in the so-called "starch-size" process inside the paper machine, e.g. in a sizing press, or
- (B) in the so-called "pigment coating" process, inside or out of the paper machine.

For the starch-size process according to (A), a coating liquor is used which, per litre, contains, e.g. 0.2 to 2.0 g. of optical brightener of Formula I and 50–100 g. of degraded starch. In addition it can contain slight amounts of wetting agents, e.g. unsulphated or sulphated alkanol glycol ethers having an alkyl radical containing 8–14 carbon atoms and having 1 to 20 ethylene oxy groups.

For the pigment coating process according to (B), a coating liquor is used which contains, per litre, e.g. 0.2–5.0 g. of optical brightener of Formula I, 350–650 g. of white pigment and, calculated on the amount of white pigment used, 8–30% by weight of binder, 0.2–0.6% by weight of metal binding agents and 0.01–0.03% by weight of wetting agents.

Examples of white pigments are aluminum-magnesium silicate (China Clay),  $\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$  (Satinweiss),  $\text{BaSO}_4$  (Blancfix), titanium dioxide, optionally also  $\text{CaCO}_3$ , or mixtures of such compounds.

Examples of binders are dispersions of synthetic resins such as those based on butadiene-styrene, acrylic or methacrylic polymers or copolymers, together with degraded starch, or dispersions of synthetic resins with casein, or such dispersions together with degraded starch and casein.

Examples of metal binding agents are water soluble polyphosphates or polymetaphosphates, and examples of wetting agents are unsulphated or sulphated higher alkanol-polyglycol ethers such as those mentioned in the previous paragraph.

In order to obtain good rheological properties, preferably an alkaline coating liquor is used for pigment coating. The alkaline reaction is advantageously adjusted with ammonium hydroxide or with sodium or potassium hydroxides, carbonates, borates, perborates or mixtures thereof.

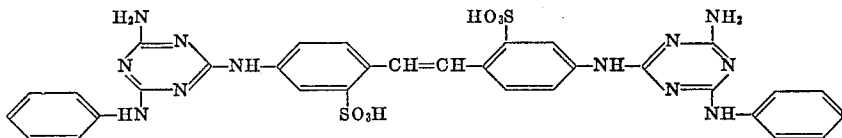
Paper is advantageously coated with these liquors according to (A) and (B) in a painting apparatus used for this purpose. In this way papers are obtained which, in addition to an improved surface, have a more white and pleasant appearance.

The following examples illustrate the invention. The temperatures are given there in degrees centigrade.

## EXAMPLE 1

Brightening in the starch-size process

2 g. of optical brightener of the formula



as disodium salt are dissolved in 40 ml. of 90° hot, distilled water.

Also 80 g. of a degraded starch (e.g. Noredux 100®, Blattmann Co., Wädenswil, ZH, Switzerland) in 1000 ml. of 90° hot water are made into a colloid suspension over a period of 15 minutes.

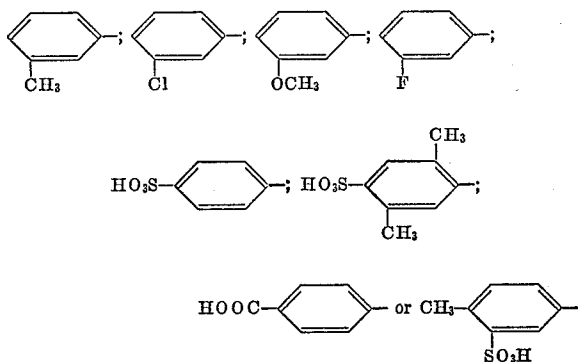
The brightener solution is then incorporated into the starch solution. The solution obtained containing starch and brightener has a pH of 5.5 to 6.0.

The surface of a sized paper for printing is coated with this liquor in a sizing press and the coated paper is dried at about 50-120° in the drier section of the paper machine.

In this way a paper is obtained the degree of whiteness of which is considerably improved.

Instead of sized paper, sized cardboard can be used with the same result.

Similar results are obtained under otherwise the same conditions if, instead of the brightener given above, a brightener of similar structural formula is used which, instead of the phenyl substituent corresponding to Ar in general Formula I, contains one of the radicals:



(1)

## EXAMPLE 2

Brightening in the pigment coating process

3.5 g. of the optical brightener given in paragraph 1 of Example 1 are dissolved in 40 ml. of 90° hot, distilled

water. 1000 ml. of an aqueous coating liquor are then added to this solution, which liquor contains the following components:

25	Usual commercial casin.....g--	45
	A dispersion of synthetic resin containing about 50% synthetic resin, based on butadiene-styrene polymers (e.g. Dow-Latex 636®, Dow Chem. USA).....g--	70
30	Sodium polyphosphate.....g--	2
	Sulphated dodecyl alcohol polyglycol ether having 15 ethylene oxy groups.....ml--	0.2
	Aluminum-magnesium silicate ("China clay") ..g--	400
	Concentrated ammonia.....ml--	12

35 The pH of this dispersion is about 9.0.

The surface of sized paper or cardboard is coated with this liquor in the sizing press or another device.

A paper coated extraordinarily white is obtained.

## EXAMPLE 3

Brightening of paper pulp

50 g. of an aqueous suspension of bleached sulphite cellulose containing 5 g. of absolutely dry cellulose are mixed with 100 ml. of water and the mixture is stirred well at room temperature. 0.71 ml. of a sizing solution 1:10 is added and the whole is again well mixed. 5 mg. of the optical brightener described in paragraph 1 of Example 1, dissolved in 10 ml. of water, are then mixed in, the mixture is again stirred well whereupon the brightener completely draws onto the cellulose fibres. 1.5 ml. of aluminum sulphate solution 1:10 are then added to the pulp which is subsequently diluted with water to 1000 ml.

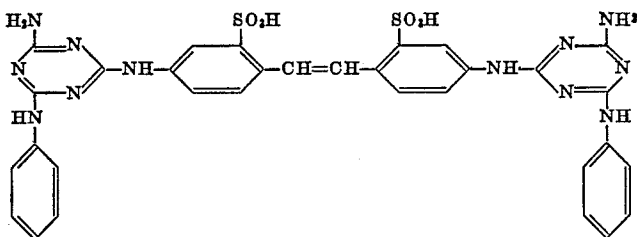
55 The diluted pulp is made into sheets, pressed and dried. In this way a clear, white sheet is obtained.

Similar results are attained when the brighteners mentioned in the last paragraph of Example 1 are used.

We claim:

1. An aqueous coating liquor for the optical brightening of the surface of paper, said coating liquor comprising, per liter,

(a) 0.2 to 2.0 g. of a compound of the formula:



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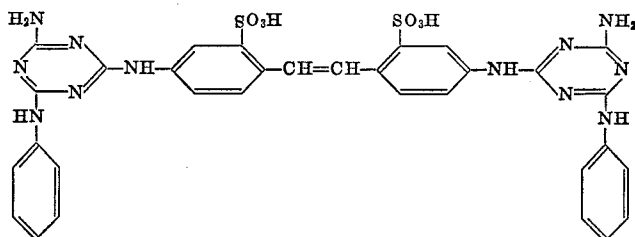
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- (ii) water soluble salts of the compound (i); and  
(b) 50 to 100 g. of degraded starch.

(i)

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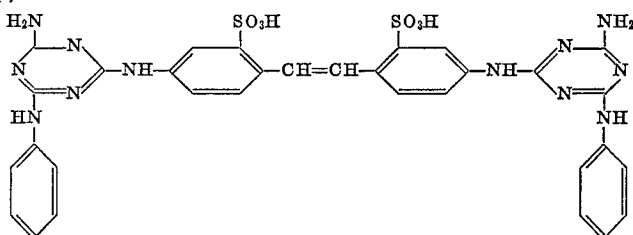
- (a) 0.2 to 2.0 g. of a compound of the formula:



2. An aqueous coating liquor for the optical brightening of the surface of paper, said liquor comprising, per liter:

- (a) 0.2 to 5.0 g. of an optical brightener of the formula:

(i)



- (ii) water soluble salts of the compound (i);  
(b) 350 g. to 650 g. of a white pigment selected from the group consisting of China clay,  $\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{BaSO}_4$  or  $\text{TiO}_2$ , or mixtures thereof;

(i)

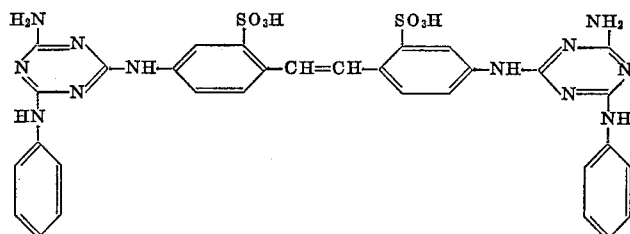
- (ii) water soluble salts of the compound (i); and  
(b) 50 to 100 g. of degraded starch.

5. A method as claimed in claim 4 wherein the compound is disodium 4,4'-bis[(4-anilino-6-amino-1,3,5-triazine-2-yl)-amino]-stilbene-2,2'-disulfonate.

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6. A method as claimed in claim 4 wherein said liquor comprises, per liter,

- (a) 0.2 to 5.0 g. of an optical brightener of the formula:



- (c) 8-30% by weight of a binder based upon the weight of said pigment;

- (d) 0.2 to 0.6% of a metal binding agent based upon the weight of said pigment; and

- (e) 0.01 to 0.3% of wetting agents based upon the weight of said pigment.

3. A coating liquor as claimed in claim 2 wherein said binder is a dispersion of a synthetic resin selected from the group of butadiene-styrene, acrylic or methacrylic polymers and copolymers, and mixtures thereof with casein.

4. A method for brightening the surface of paper comprising coating the surface of the paper with an amount to effectively optically brighten said surface of said paper with an aqueous coating liquor comprising, per liter,

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- (ii) water soluble salts of the compound (i);

- (b) 350 g. to 650 g. of a white pigment selected from the group consisting of china clay,  $\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{BaSO}_4$  or  $\text{TiO}_2$ , or mixtures thereof;

- (c) 8-30% by weight of a binder based upon the weight of said pigment;

- (d) 0.2 to 0.6% of a metal binding agent based upon weight of said pigment; and

- (e) 0.01 to 0.3% of wetting agents based upon the weight of said pigment.

7. A method as claimed in claim 6 wherein the compound is disodium - 4,4'-bis[(4-anilino-6-amino-1,3,5-triazine-2-yl)-amino]-stilbene-2,2'-disulfonate.

#### References Cited

##### UNITED STATES PATENTS

2,376,743	5/1945	Wendt	106-162
2,213,643	9/1940	Acton	260-8 X

##### FOREIGN PATENTS

529,326	8/1956	Canada.
862,851	3/1961	Great Britain.

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117-33.5, 156; 252-301.2