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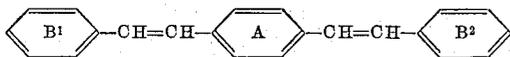
3,294,570

**OPTICAL BRIGHTENING OF MATERIALS OF SYNTHETIC POLYESTERS AND POLYAMIDES**

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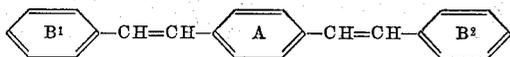
This invention relates to the optical brightening of materials of synthetic linear polyesters and polyamides by surface treatment with p-bis-styryl-benzene:



and derivatives thereof sparingly soluble in water and bearing substituents on the benzene rings A, B<sup>1</sup> and B<sup>2</sup>.

Austrian patent specification No. 220,831 describes mass optical brightening of plastics of all types with the said compounds. Furthermore it is known from U.S. patent specification No. 3,076,020 that certain water-soluble derivatives of this class of compounds may be used for the bath treatment of textiles. The best results are achieved with cotton and also with polyamides, but in the latter case the stability of the brightening leaves to be desired.

We have now found that materials of synthetic linear polyesters and polyamides can be durably brightened by surface treatment from aqueous baths or by means of print pastes by using for the purpose aqueous dispersions of p-bis-styryl-benzene:



or derivatives thereof which are sparingly soluble in water and bear substituents on the benzene A, B<sup>1</sup> and B<sup>2</sup> and which have a fluorescence maximum between 390 and 450 millimicrons, and then fixing these compounds on the substrate at temperatures of 90° to 225° C., preferably at 140° to 200° C. By fixing we understand heating the polyester or polyamide material, after it has been treated with the lightening liquor at the said temperatures.

Among the compounds suitable for the process according to this invention (which may be obtained as described in German patent specification No. 1,122,524, U.S. patent application Serial No. 28,546, filed May 12, 1960, by Walter Stilz and Horst Pommer, and British Patents Nos. 920,988 and 929,436) those are most active which have fluorescence maxima in the ultraviolet range between about 390 and 450 millimicrons (measured in dioxane). Compounds of this type are for example those in which the rings A, B<sup>1</sup> and B<sup>2</sup> are substituted as follows, and also mixtures of these compounds, and among these particularly mixtures obtained by synthesis when the initial compounds corresponding to the parts B<sup>1</sup> and B<sup>2</sup> of the molecule are different.

2

The substituents in rings A, B<sup>1</sup> and B<sup>2</sup> may be:

	A	B <sup>1</sup> and B <sup>2</sup>
1	Unsubstituted	2-chloro-
2	do	2-bromo-
3	do	2,4-dichloro-
4	do	2,6-dichloro-
5	do	3,4-dichloro-
6	do	2-cyano-
7	do	3-cyano-
8	do	4-cyano-
9	do	3-chloro-4-cyano-
10	do	3-chloro-6-cyano-
11	do	4-methyl-
12	do	2-carbomethoxy-
13	do	4-carbomethoxy-
14	do	2-methoxy-
15	do	4-methoxy-
16	do	3,4-methylenedioxy-
17	2,5-dichloro-	Unsubstituted
18	2,5-dichloro-	4-methyl-
19	2,5-dichloro-	2-chloro-
20	2,5-dichloro-	4-chloro-
21	2,5-dichloro-	2,6-dichloro-

The names of the compounds above tabulated are, in consecutive order,

- 25 p-bis-(2-chlorostyryl)-benzene,
- p-bis-(2-bromostyryl)-benzene,
- p-bis-(2,4-dichlorostyryl)-benzene,
- p-bis-(2,6-dichlorostyryl)-benzene,
- 30 p-bis-(3,4-dichlorostyryl)-benzene,
- p-bis-(2-cyanostyryl)-benzene,
- p-bis-(3-cyanostyryl)-benzene,
- p-bis-(4-cyanostyryl)-benzene,
- p-bis-(3-chloro-4-cyanostyryl)-benzene,
- 35 p-bis-(3-chloro-6-cyanostyryl)-benzene,
- p-bis-(4-methylstyryl)-benzene,
- p-bis-(2-carbomethoxystyryl)-benzene,
- p-bis-(4-carbomethoxystyryl)-benzene,
- p-bis-(2-methoxystyryl)-benzene,
- 40 p-bis-(4-methoxystyryl)-benzene,
- p-bis-(3,4-methylenedioxy-styryl)-benzene,
- p-bis-styryl-2,5-dichlorobenzene,
- p-bis-(4-methylstyryl)-2,5-dichlorobenzene,
- p-bis-(2-chlorostyryl)-2,5-dichlorobenzene,
- 45 p-bis-(4-chlorostyryl)-2,5-dichlorobenzene, and
- p-bis-(2,6-dichlorostyryl)-2,5-dichlorobenzene.

Among these compounds, those are stressed which bear cyano groups as substituents in 2- and 4-position in the outer rings.

This list is by no means exhaustive and the compounds may bear a great variety of substituents on the middle benzene ring A and on the two outer benzene rings B<sup>1</sup> and B<sup>2</sup>. Prominent among these are chlorine and bromide atoms and cyano, alkyl, alkoxy, alkyloxy, alkyloyloxy, carbalkoxy, alkylcarbonyl and dialkylcarbonyl groups, the alkyl radicals in these groups preferably containing up to four carbon atoms. The outer rings may moreover be components of polynuclear isocyclic or heterocyclic aromatic radicals.

Provided the compounds remain sparingly soluble in water, for example hydroxyl, hydroxyalkyl, amino, alkyl-amino, carbonyl and sulfonamido groups may also be substituents.

Suitable substrates are shaped articles of all types, for example films, sheeting, filaments, threads and staple fibres and above all plane textile materials of linear synthetic polyamides and polyesters. Polycaprolactam, polycaprylactam and polyadipic hexamethylene diamide may be emphasized among the polyamides and polyethylene glycol terephthalate among the polyesters.

The said compounds may be applied to the substrates, for example textile material, by various methods. They are particularly well suited to the thermosol method, the high-temperature exhaustion method and the exhaustion method at 100° C.

In all these methods, the said compounds are advantageously brought before use into a state of fine division, for example by grinding with dispersing agents, such as soaps, sulfite cellulose waste liquor, polyglycol ethers of fatty alcohols or fatty amines or condensation products of naphthalenesulfonic acids substituted naphthalenesulfonic acids and formaldehyde. The treatment liquor may be alkaline, neutral or, preferably, acid. The amount of optical brightener, with reference to the amount of liquor, may vary within wide limits. Even with very small amounts, in certain cases for example amounts as low as 0.01 g./l., a marked and durable effect can be achieved. Although amounts of more than 10 g./l. have not proved in general to be disadvantageous, they usually do not offer any advantage over the normal amounts.

In the thermosol method, the material to be treated is padded, preferably on a padding machine, with an aqueous dispersion of the optical brightener, which may contain thickeners such as are conventionally used in printing. The material is then dried and subjected to a hot air treatment. The temperature of fixation depends on the composition of the material. In the case of polyesters it may be 120° to 220° C. and in the case of polyamides 120° to 200° C. Following this treatment, the material is rinsed and soaped as usual.

Another embodiment consists in effecting fixation with superheated steam at temperatures between about 100° C. and 140° C. instead of with hot air. This method also gives materials showing an outstanding optical brightening effect.

The high-temperature exhaustion method is treatment of the material to be brightened for a long period and from a long liquor. A high-temperature dyeing machine is used for this purpose at temperatures above 100° C., for example at 105° to 140° C. The liquor ratio may be 5:1 to 50:1 and the residence time 30 to 60 minutes.

In the exhaustion method, the material is treated at the boiling temperature of the liquor or in the neighborhood thereof (about 90° C.). The procedure may be that the materials are introduced at 60° to 70° C. into the treatment liquor containing the optical brightener in finely divided form and the temperature is raised to 95° to 100° C. The residence time may be about thirty to sixty minutes. The material is then rinsed and dried. An outstanding optical brightening effect is achieved in this way.

Often it is very advantageous, particularly with polyesters and especially with polyester fibers, to use carriers to accelerate absorption and exhaustion of the treatment liquid. Examples of suitable carriers are dichlorobenzene, trichlorobenzene, o-phenylphenol, p-phenylphenol, benzoic acid, the p-chlorophenyl monoether of glycol and esters of benzoic acid.

In general it is advantageous to add to the liquors dispersing agents, such as soaps, polyglycol ethers and the like so that the brightener remains finely dispersed in the liquor.

It is often possible to apply the brightener and a disperse dye from one and the same liquor.

Another embodiment of the process according to this invention consists in applying the optical brightener, if desired with a disperse dye, to the material to be brightened in the form of a print paste by means of the usual

printing methods. Fixation is then effected in exactly the same way as described above.

The said methods, which in general cover the conventional methods of dyeing polyesters and polyamides with disperse dyes, may without difficulty be transferred to the treatment of filaments, threads, staple fibers, films, sheeting and other shaped articles.

The unforeseeable good results of the process according to this invention, which consist in the optical brightening in a way which is very light fast and resistant to mechanical and chemical influences, both of polyesters and polyamides, are particularly remarkable in the case of polyesters because these materials are known to have only slight affinity to other substances. A particular advantage of the optical brighteners to be used according to this invention is that they are stable to solutions of bleaching agents, such as sodium chlorite. Optical bleaching and chemical bleaching may therefore be carried out in one operation.

The invention will be further illustrated by the following examples. The parts and percentages are by weight.

#### Example 1

100 parts of a washed polyester cloth is treated for thirty minutes at 98° C. in a liquor containing 3000 parts of water, 0.15 part of the optical brightener 3 in the foregoing table which is in a state of fine division and 1.7 parts of formic acid. The cloth is rinsed and dried as usual. A polyester cloth showing an outstanding optical brightening effect and very good light and wash fastness is obtained.

#### Example 2

100 parts of polyester cloth is treated for sixty minutes at 98° C. in a liquor which contains 3000 parts of water, 0.15 part of optical brightener 17 in the foregoing table which is in a state of fine division and 2.4 parts of sodium chloride and 0.6 part of the sodium salt of oleic acid tauride, 1 part of tetrasodium pyrophosphate and 0.6 part of sodium acetate. The pH value of the liquor is adjusted with formic acid to 3 to 4 prior to introduction of the cloth. The cloth is rinsed and dried. The treated cloth has a brilliant white appearance.

#### Example 3

100 parts of polyester yarn is treated for sixty minutes at 98° C. in a liquor containing 3000 parts of water, 12 parts of a mixture of dichlorobenzene and trichlorobenzene and 0.1 part of the brightener 7 in the foregoing table. The polyester yarn obtained after rinsing and drying shows an outstanding optical brightening effect.

#### Example 4

100 parts of a washed polyester cloth is treated for thirty minutes at 130° C. in a liquor containing 3000 parts of water and 0.2 part of brightener 13 in the above table in a state of fine division. The product is rinsed and dried and polyester cloth showing an outstanding optical brightening effect and very good light and wash fastness is obtained.

#### Example 5

A polyester cloth is padded at room temperature with a solution containing, in 1000 parts of water, 3 parts of the optical brightener 8 in the above table in a state of fine division. Liquor take-up is 50%. The cloth is dried at 60° C. and subjected to a hot air treatment at 180° C. for three minutes. The cloth is then soaped with 2 g./l. of soap for thirty minutes at 80° C. at a liquor ratio of 50:1, rinsed and dried. A polyester cloth showing an outstanding optical brightening effect and very good light and wash fastness is obtained.

#### Example 6

A polyamide cloth is padded at room temperature with a solution containing 2.5 parts of the optical brightener 6 in the above table in a state of fine division in 1000

5

parts of water. The liquor retention is 40%. The cloth is dried at 60° to 70° C. and then subjected to a hot air treatment at 180° C. for three minutes. The cloth is then soaped with 2 g./l. of soap at a liquor ratio of 50:1 for thirty minutes at 70° to 80° C. and then rinsed and dried. A polyamide cloth showing an excellent optical brightening effect and good fastness to light is obtained.

#### Example 7

A polyester cloth is padded at room temperature with a solution containing, in 1000 parts of water, 2 parts of a finely divided brightener mixture of about 50% of 1-(2-cyanostyryl)-4-(4-cyanostyryl)-benzene, 25% of 1,4-bis-(2-cyanostyryl)-benzene and 25% of 1,4-bis-(4-cyanostyryl)-benzene. Liquor retention is about 60%. The cloth is then dried and subjected to a hot air treatment at 190° C. for three minutes. It is then soaped and dried. A polyester cloth showing an outstanding optical brightening effect and very good wash fastness is obtained.

We claim:

1. A process for the optical brightening of a material selected from the group consisting of synthetic linear polyesters and synthetic linear polyamides which comprises treating said material by applying thereto an aqueous dispersion in which is dispersed an optical brightener which is sparingly soluble in water and consisting essentially of a member selected from the group consisting of

p-bis-styryl-benezne,  
 p-bis-(2-chlorostyryl)-benzene,  
 p-bis-(2-chlorostyryl)-benzene,  
 p-bis-(2-bromostyryl)-benzene,  
 p-bis-(2,6-chlorostyryl)-benzene,  
 p-bis-(3,4-dichlorostyryl)-benzene,  
 p-bis-(2-cyanostyryl)-benzene,  
 p-bis-(3-cyanostyryl)-benzene,  
 p-bis-(4-cyanostyryl)-benzene,  
 p-bis-(3-chloro-4-cyanostyryl)-benzene,  
 p-bis-(3-chloro-6-cyanostyryl)-benzene,

6

p-bis-(4-methylstyryl)-benzene,  
 p-bis-(2-carbomethoxystyryl)-benzene,  
 p-bis-(4-carbomethoxystyryl)-benzene,  
 p-bis-(2-methoxystyryl)-benzene,  
 p-bis-(4-methoxystyryl)-benzene,  
 p-bis-(3,4-methylenedioxytyryl)-benzene,  
 p-bis-styryl-2,5-dichlorobenzene,  
 p-bis-(4-methylstyryl)-2,5-dichlorobenzene,  
 p-bis-(2-chlorostyryl)-2,5-dichlorobenzene,  
 p-bis-(4-chlorostyryl)-2,5-dichlorobenzene, and  
 p-bis-(2,6-dichlorostyryl)-2,5-dichlorobenzene,

and mixtures thereof and fixing said brightener on said material by heating the treated material at a temperature between 90° C. and 215° C.

2. The process as claimed in claim 1 wherein said material comprises synthetic linear polyester fibers and an accelerator is employed to accelerate absorption of said compound by said fibers and thereby exhaustion of said aqueous dispersion.

3. A process as claimed in claim 1 wherein superheated steam at 100-140° C. is applied to said treated material to effect said fixing.

4. A process as claimed in claim 1 wherein hot air at 120-225° C. is applied to said treated material to effect said fixing.

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