

[54] **PROCESS FOR THE OPTICAL BRIGHTENING OF ORGANIC FIBRE MATERIAL**

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[63] Continuation-in-part of Ser. No. 72,210, Sept. 14, 1970, abandoned.

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[51] Int. Cl..... C09k 1/02

[58] Field of Search 252/301.2 W; 117/33.5 T, 117/139.5 CQ; 260/240 C

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[57] **ABSTRACT**

A process for the non-aqueous optical brightening of organic fibre material, especially fibre material made from cellulose, natural or synthetic polyamide, by the exhaustion method, is disclosed, which comprises treating said fibre material in the solution of at least one optical brightener salt consisting of the anionic radical of an anionic optical brightener and at least one cationic radical of an inorganic or organic base, said organic base being derived from an organic nitrogen compound containing at least one nitrogen atom capable of salt formation, in a solvent mixture consisting of unsubstituted or halogenated hydrocarbon boiling between 50° and 150°C and liquid, water soluble organic solvent boiling below 220°, at a temperature between room temperature and the boiling point of the solvent mixture, optionally under pressure, and finishing the brightened fibre material in the usual manner. By this process, excellent white-effects or brightenings having good fastness properties, such as fastness to dry cleaning and washing, are obtained on said fibre material, without any subsequent heat treatment such as steaming or thermofixing.

10 Claims, No Drawings

PROCESS FOR THE OPTICAL BRIGHTENING OF ORGANIC FIBRE MATERIAL

This application is a continuation-in-part of copending Ser. No. 72,210, filed on Sept. 14, 1970, now abandoned.

The present invention relates to a process for the non-aqueous optical brightening of organic fibre material, especially fibre material from cellulose, natural or synthetic polyamide, in an organic solvent mixture, as well as the fibre material brightened according to this process.

It is known that fibre material of incompletely acylated cellulose can be brightened continuously using, inter alia, optical brighteners, containing sulphonic acid groups, in the form of their sodium salts, by impregnating this fibre material with the solution of an optical brightener in a water-soluble organic solvent, such as lower alkanols, optionally mixed with a water-insoluble organic solvent preferably boiling below 250°C, and removing the excess solvent from the material under mild conditions, preferably at temperatures between 30° and 100°C. This process is disadvantageous inasmuch as with it satisfactory brightening effects can practically only be achieved on cellulose 2½-acetate.

It has been found that excellent white-effects or brightenings can be obtained on organic fibre material, particularly on cellulose fibres, and natural and synthetic polyamide fibres without subsequent heat treatment such as steaming or thermofixing, when the organic fibre material is treated by the exhaustion process in a goods to liquor weight ratio of at least 1:5 in the solution of at least one optical brightener salt consisting of the anionic radical of an anionic optical brightener and at least one cationic radical of an inorganic or organic base, said organic base being derived from an organic nitrogen compound which contains at least one nitrogen atom capable of salt formation, in a solvent mixture which consists of from 50 to 99 percent by weight of unsubstituted or, preferably, halogenated hydrocarbon boiling between 50° and 150° C and from 50 to 1 percent by weight of liquid, water-soluble organic solvent boiling below 220°C, at a temperature between room temperature and the boiling point of the solvent mixture, optionally under pressure, but preferably at a temperature of from 30° to 75°C, and finishing the brightened fibre material in the usual manner.

In comparison with the previously known continuous process, more brilliant and intense brightening effects are in particular achieved, according to the invention, on cotton and fibre material of synthetic polyamide, whilst, on the other hand, the process according to the invention is distinguished, relative to the known aqueous application from a long bath, by better development of the brightener salts (higher fluorescence counts and more intense, more brilliant white effects) at low bath temperatures (approx. 20° to 50°C).

Suitable brightener salts which can be used according to the invention as the salts of inorganic bases, are preferably the alkali metal salts, such as the potassium, lithium or especially the sodium salts, or the ammonium salts of an anionic optical brightener, especially of an optical brightener containing sulphonic acid groups and/or carboxylic acid groups. The brightener salts obtained industrially can be used directly. They can also be manufactured in a manner which is in itself known, for example by neutralisation of the aqueous solution

of the anionic optical brighteners in the form of their free sulphonic acids and/or carboxylic acids, with appropriate inorganic bases, such as, for example, alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates or ammonia. The brightener salts can also be manufactured in situ, for example by directly introducing the optical brighteners, in the form of their free sulphonic acids and/or carboxylic acids, into an alkali alcoholate solution, advantageously into a sodium methylate solution.

The nitrogen atom, capable of salt formation, of the organic nitrogen bases usable according to the invention, can be in the form of a primary, secondary, tertiary or quaternary amino group. Examples of particularly suitable compounds are as follows:

1. Substituted or unsubstituted aliphatic amines, especially alkylamines, such as butylamine, hexylamine, octylamine, decylamine, dodecylamine, tetradecylamine, octadecylamine, diethylamine, dibutylamine, dioctylamine, didodecylamine, N-methyl-N-dodecylamine, N-ethyl-N-octadecylamine, triethylamine, tributylamine, N,N-dimethyl-N-dodecylamine, N,N-dimethyl-N-octadecylamine, β -hydroxyethyl-amine, γ -hydroxypropylamine, N- β -hydroxyethyl-N-dodecylamine, γ -methoxypropylamine, N- γ -methoxypropyl-N-dodecylamine, N- γ -hydroxyethyl-N-octadecylamine, N,N-dimethyl-N-benzyl-dodecylammoniumhydroxide, N,N,N-trimethyl-dodecylammonium hydroxide and trimethyl-dodecylammonium hydroxide.

2. Substituted or unsubstituted aliphatic di- and triamines such as 1,2-ethylenediamine, 1,3-propylenediamine, diethylenetriamine, 1,1-bis-methylpropylenediamine, 1,1-bis-dodecylpropylenediamine, 1,1-bis-cyclohexyl-propylenediamine, 1,1-bis-benzylpropylenediamine, N,N'-bis-phenylethylenediamine, N,N,N',N'-tetrapropylpropylenediamine, N,N,N',N'-tetrabenzylpropylenediamine, N,N,N',N'-tetra- β -hydroxyethylpropylenediamine, 1-dodecylethylenediamine, 1-octadecyl-ethylenediamine and 1-octadecyldiethylenetriamine.

3. Substituted or unsubstituted cycloalkylamines such as cyclohexylamine, N-methylcyclohexylamine, N-octylcyclohexylamine, N- β -hydroxyethylcyclohexylamine, N-methyl-N- γ -hydroxyethylcyclohexylamine, dicyclohexylamine, dehydroabietylamine and trimethylcyclohexylammonium hydroxide.

4. Substituted or unsubstituted aralkylamines such as benzylamine, β -phenylethylamine, N- β -hydroxyethylbenzylamine, N- γ -methoxypropylbenzylamine, N- β -cyanoethylbenzylamine, N-methyl-N- γ -methoxypropylbenzylamine, N-octylbenzylamine, N-octadecylbenzylamine and dibenzylamine.

5. Substituted or unsubstituted aromatic amines, especially mononuclear aromatic amines such as aniline, N-methylaniline, N,N-dimethylaniline, N,N-dibutylaniline, N- β -hydroxyethyl-N-methylaniline and toluidine.

6. Unsubstituted or substituted amidines, especially alkylamidines, such as acetamidine, benzamidine, laurylamidine, stearylaminidene, as well as N-methyl-laurylamidine, N-butyl-laurylamidine, N-phenyl-laurylamidine, N-benzyl-laurylamidine, N-methylstearylaminidene, N-benzylstearylaminidene, or N-cyclohexylstearylaminidene.

7. Substituted isothioureas, preferably S-alkyl-isothioureas, such as S-benzyl-isothiourea, S-methyl-, S-butyl-, S-hexyl-, S-octyl-, S-undecyl-, S-dodecyl- and S-octadecyl-isothiourea.

8. Guanidines, especially alkylguanidines, such as phenylguanidine, benzylguanidine, dodecylguanidine and octadecylguanidine.

9. Hydrazines such as phenylhydrazines or undecyl-hydrazine.

10. N-containing five- or six-membered heterocycles which can be partially or completely saturated.

Examples of five-membered N-containing heterocycles are: pyrroles such as methylpyrrole and benzylpyrrolé; pyrrolines such as methylpyrroline or benzyepyrroline; also pyrrolidines such as methylpyrrolidine, butylpyrrolidine or dodecylpyrrolidine; pyrazoles; pyrazolines such as N-methylpyrazoline; pyrazolidines, especially unsubstituted or substituted 2-alkylimidazolines, such as 2-heptylimidazoline, 2-undecylimidazoline, 2-heptadecylimidazoline, 1-methyl-2-undecylimidazoline, 1- β -hydroxyethyl-2-undecylimidazoline, 1- β -hydroxyethyl-2-heptadecylimidazoline, 2-aminoethyl-1-heptadecylimidazoline, 3,5-diamino-1,2,4-triazole and 3,5-diamino 1,2,4-phenyltriazole.

Examples of six-membered N-containing heterocycles are: piperidine and its derivatives, especially N-alkyl or N-aralkyl-piperidine such as N-methylpiperidine, N-dodecylpiperidine and N-benzylpiperidine; piperazines such as N-octadecylpiperazine; morpholine and, in particular, its N-alkyl and N-aralkyl derivatives such as N-butymorpholine, N-octadecylmorpholine or N-benzylmorpholine; quinclidine and pyridine, N-methyl-pyridinium hydroxide and octadecyloxy-methylenepyridinium hydroxide; pyrimidines such as dihydro- and especially tetrahydro-pyrimidines, preferably 2-alkyltetrahydropyrimidines, such as 2-heptyl-tetrahydropyrimidine, 2-undecyl-tetrahydropyrimidine, 2-heptadecyltetrahydropyrimidine, 1-methyl-2-undecyl-tetrahydropyrimidine or 1- β -hydroxyethyl-2-heptadecyl-tetrahydropyrimidine, 2-amino-1-octadecyl-tetrahydropyrimidine; 1,3,5-triazines, particularly derivatives of the 2,4,6, -triamino-1,3,5-triazine such as 2-dodecylamino-4,6-bis-amino-1,3,5-triazine or 2-octadecylamino-4,6 -bis-amino-1,3,5-triazine, 2-heptadecyl-4,6-bis-amino-1,3,5-triazine; or hexahydro-1,3,5-triazine derivatives.

11. Condensed N-containing heterocycles such as indolines and indoles.

Preferred organic nitrogen compounds are alkylamines having preferably from 12 to 18 carbon atoms in the alkyl radical such as dodecylamine and octadecylamine; alkylguanidines having preferably from 12 to 18 carbon atoms in the alkyl radical such as dodecylguanidine or octadecylguanidine; S-benzyl-isothiourea or S-alkyl-isothioureas having preferably from 11 to 18 carbon atoms in the alkyl radical such as S-undecyl-, S-dodecyl- and S-octadecyl-isothiourea; and, particularly, 2-alkylimidazolines and 2-alkyltetrahydropyrimidines having preferably from 11 to 18 carbon atoms in the alkyl radical such as 1-undecyl-imidazoline, 2-heptadecyl-imidazoline, 2-undecyl-tetrahydropyrimidine and 2-heptadecyl-tetrahydropyrimidine and their 1-alkyl derivatives.

Advantageously salts from an optical brightener containing carboxylic acid, or, especially, sulphonic acid

groups and an organic nitrogen compound as defined are used. The anionic optical brighteners can belong to very diverse classes. Particularly brilliant brightening effects are obtained with compounds which are derived from the lasses of the stilbenes and pyrazolines. Suitable derivatives from these classes are preferably those of distyryl-diphenyl-disulphonic acids, 4,4'-bis-triazinylaminostilbene-sulphonic acids, stilbylnaphthotriazolecarboxylic acids or -sulphonic acids, 4,4'-bis-triazolylstilbene-sulphonic acids or derivatives of diarylpyrazolines and triarylpyrazolines, containing carboxylic acid or sulphonic acid groups. Derivatives of dibenzthiophenedioxides such as those containing sulfonic acid groups are mentioned as further suitable brighteners.

Suitable hydrocarbons, boiling between 50° and 150°C are, e.g., aromatic hydrocarbons such as toluene or xylene. Preferably, however, halogenated, especially chlorinated hydrocarbons are used, e.g., chlorobenzene, but particularly, on account of their generally better regeneration property and non-combustibility, lower aliphatic halogenated hydrocarbons, especially chloro-, bromo-, fluoro- or fluoro-chloro-hydrocarbons, e.g., tri- or tetrachloroethylene ("perchloroethylene"), 1,1,2-trifluoro-1,2,2-trichloroethane, dichloroethane, 1,1,1-trichloroethane, tetrachloroethane, pentafluoroethane, dibromoethylene, tribromoethylene, chloroform or carbon tetrachloride. It is also possible to use mixtures of such solvents.

By "liquid, water-soluble, organic solvents boiling below 220°C" are meant thermostable solvents which are soluble in water not to the extent of only fractions of one per cent but to the extent of several per cent. Examples of these are: higher alkanols such as butanols or amyl alcohols, cycloaliphatic alcohols such as cyclohexanol, araliphatic alcohols such as benzyl alcohol, or aliphatic or cycloaliphatic ketones such as acetone, methyl ethyl ketone or cyclohexanone. Such solvents, as defined, are preferred, however, which are miscible with water in any proportion. Examples of these are: monovalent lower aliphatic alcohols such as lower alkanols, e.g. methanol, ethanol, n- or isopropanol; alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl or monoethyl ether; also furfuryl or tetrahydrofurfuryl alcohol, lower cyclic ethers such as dioxane; lower anhydrous monocarboxylic acids such as anhydrous formic acid or propionic acid, and, especially, glacial acetic acid; N,N-dialkylamides of lower monocarboxylic acids such as dimethylformamide or dimethylacetamide, amides of carbonic acid such as N,N,N',N'-tetramethylurea, cyclic amides such as N-methylpyrrolidone, or lower carboxylic acid nitriles such as acetonitrile, as well as mixtures of such liquid, water soluble organic solvents.

The composition of the solvent mixture is governed by the solubility of the optical brightener salt or salts to be used. The composition should be such that a homogeneous and clear brightener solution is obtained.

Moreover, care must be exercised in choosing the solvent mixture that, with optimal white-effect, no damage or minimal damage to the fibres occurs.

Preferred solvent mixtures consist of 80 to 99 percent by weight of liquid, water-soluble organic solvent, in particular halogenated lower aliphatic hydrocarbon, boiling between 50° and 150°C and of 20 to 1 percent by weight of liquid, water-soluble organic solvent boil-

ing below 220°C, but more especially of 90 to 99 percent by weight of trichloroethylene, tetrachloroethylene, trichloroethane or trifluorotrichloroethane and of 10 to 1 percent by weight of a lower alkanol, such as ethanol, n- and isopropanol or n-butanol, and above all methanol; a lower N,N-dialkylamide of a lower monocarboxylic acid such as dimethylformamide or dimethylacetamide; a lower alkylene glycol monoalkyl ether, such as ethylene monoglycol methyl ether; or a lower ketone, such as acetone; or mixtures thereof.

In this specification and the appended claims, when not expressly stated otherwise, the term "lower" in connection with "alkyl" or "alkylene" designates a radical having at most 4 carbon atoms.

The brightener salts of inorganic bases which can be used according to the invention are known.

The production of the salts from the anionic optical brightener and an organic nitrogen base containing at least one nitrogen atom capable of salt formation can be performed in a known manner, e.g., by double reaction of the alkali metal or ammonium salts, particularly the sodium salts of the anionic optical brightener, advantageously at a raised temperature, with a salt of an organic nitrogen compound, usable according to the invention, and with a strong acid, e.g., hydrochloric acid, or by direct neutralisation of the anionic optical brighteners in the form of their acids with the organic nitrogen compounds. The optical brightener salts can also be prepared in situ, i.e., in a solvent mixture as defined, either by double reaction or direct neutralisation as described above. In this case, it is advantageous to remove insoluble constituents, if any, from the brightening bath, e.g., by filtration, before the introduction of the fibre material to be brightened.

When anionic optical brighteners are used which are capable of forming anions having two or more negative charges, it is often not necessary that these charges be completely compensated by the organic nitrogen compound.

Advantageously, the optical brightener salts or the optical brightener and the organic nitrogen compound are pre-dissolved in small amounts of an organic solvent as defined, such as methanol, N-methylpyrrolidone or dimethylformamide, after which the solution obtained is combined with the remaining solvent mixture.

The organic fibre material is conveniently treated in the brightener bath as defined for 5 minutes to 2 hours, especially for 15 to 45 minutes, according to the exhaustion method, at a goods: liquor ratio of from 1:5 to 1:300, particularly from 1:10 to 1:50 (calculated on parts by weight), and the brightened fibre material is then finished in the usual manner by squeezing or centrifuging etc., and drying, for example in warm air.

The brightener liquor, usable according to the invention, preferably contains, depending on the type of the optical brightener salt, from 0.01 to 2, especially from 0.1 to 0.5 percent by weight of optical brightener salt,

calculated on the dry weight of the fibre material.

Suitable organic fibre material, which can be brightened using the process according to the invention, are, amongst others, cellulose esters such as cellulose-2½-and -tri-acetate, also high-molecular esters of aromatic polycarboxylic acids with polyfunctional alcohols, e.g., polyethylene glycol terephthalate or acid-modified polyethylene glycol terephthalate, polyurethane, natural polyamides, such as wool and silk, polymeric and copolymeric acrylonitrile and methacrylonitrile, as well as polyolefins, such as polyethylene and polypropylene. The process according to the invention is, however, particularly suitable for the brightening of cellulose fibres such as viscose, and particularly, cotton, or fibre material made from natural and synthetic polyamide. Examples of fibre material made from natural polyamides are wool and silk and from synthetic polyamides are: polycaprolactam (Polyamide 6), polyhexamethylene adipic amide (Polyamide 6.6) polyundecanoic acid amide (Polyamide 11), polydodecanoic acid amide (Polyamide 12) and polyanthanic acid amide (Polyamide 7). The latter are preferably used in the form of filaments, and also in the form of texturised synthetic polyamide fibres such as "Banlon." The above-mentioned fibre material can be brightened, according to the invention, in any chosen form, e.g., in the form of flock, slubbing, yarn or — preferably — in the form of fabrics, knitted goods and so-called fully fashioned articles.

Using the process according to the invention very level and brilliant white-effects and fast optical brightenings, e.g., brightenings fast to dry cleaning and washing, are obtained on the organic fibre material, especially on cotton and synthetic polyamide fibre material.

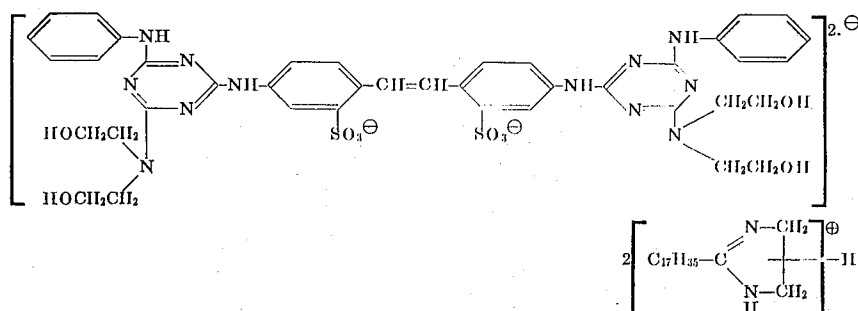
Brightenings obtained according to the process of this invention with optical brightener salts as defined from organic solvents at temperatures of, e.g., room temperature to 75°C are distinguished by improved white-effects with respect to analogous brightenings obtained under the same conditions with the corresponding sodium salts from an aqueous medium.

Since the technical carrying out of the process enables the solvents used to be recovered and used again in the brightening process, contrary to previously known processes from an aqueous medium, there is no problem of waste water purification. Furthermore, rinsing baths are not necessary, which constitutes a further advantage of the process according to the invention. The process according to the invention also makes it possible in a simple manner to combine the dry cleaning of textiles with an optical brightening.

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

EXAMPLE 1

250 milligrams of the optical brightener salt of the formula



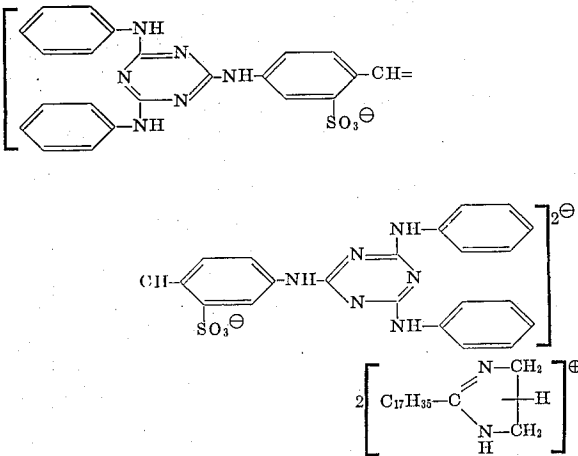
are dissolved in 10 g of methanol. The resulting solution is added to 2,000g of a solvent mixture consisting of 97 percent by weight of perchloroethylene and 3 percent by weight of methanol. At 40°, 100 g of Polyamide 6 fabric are introduced into the clear fluorescent solution obtained, and the textile material is treated therein during 30 minutes at this temperature while being moved continuously. The brightened fabric is then squeezed out and dried in warm air.

The thus treated Polyamide 6 fabric exhibits an even and brilliant white-effect.

If in the above Example with otherwise the same procedure, instead of Polyamide 6 fabric a fabric made from Polyamide 6.6, Polyamide 12 or bleached cotton is used, a brilliant white-effect is obtained also on these materials.

EXAMPLE 2

25 mg of the optical brightener salt of the formula



are dissolved in 0.5 g of N-methylpyrrolidone. The obtained clear solution is added to 150 g of a solvent mixture consisting of 97 percent by weight of perchloroethylene and 3 percent by weight of methanol. Then 10 g of Polyamide 6.6 fabric are introduced into the solution which has been heated to 35°, and the textile material is treated at the same temperature for 30 minutes while being continuously moved. The brightened fabric is then squeezed out and dried in warm air.

The thus treated fabric exhibits a brilliant, even white-effect.

If in the above Example, with otherwise the same procedure instead of a fabric made from Polyamide 6.6 a fabric made from bleached cotton or a fabric made from partially acylated cellulose is used, a brilliant, strong white-effect is obtained also on these materials.

If, instead of the brightener salt given in the above Example, the same amount of one of the brightener salts given in the following Table I, column 2, is used, the procedure being otherwise as described in the Example, then similar brightening effects are obtained on said textile materials.

TABLE I

Optical brightener salts

3		
4		
5		

TABLE I—Continued

Example number	Optical brightener salts
6.....	
7.....	
8.....	
9.....	
10.....	
11.....	

TABLE I—Continued

Example number Optical brightener salts

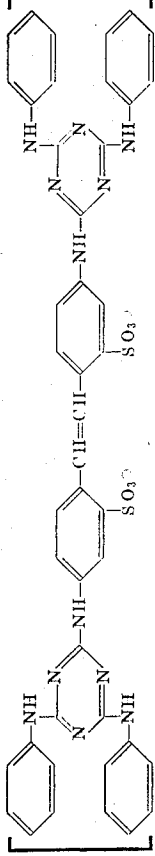
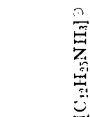
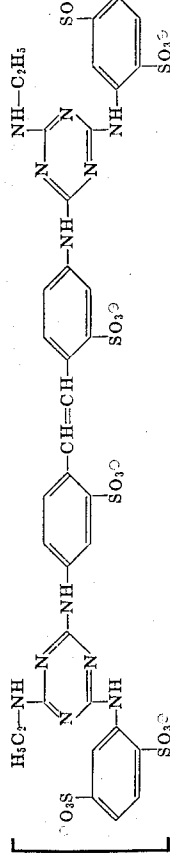
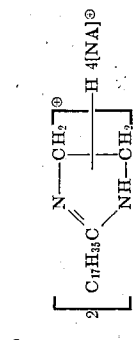
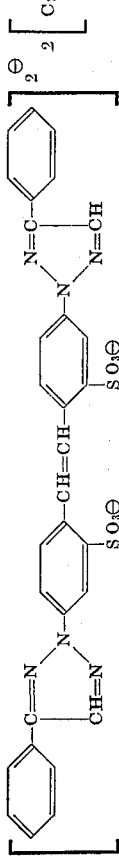
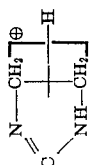
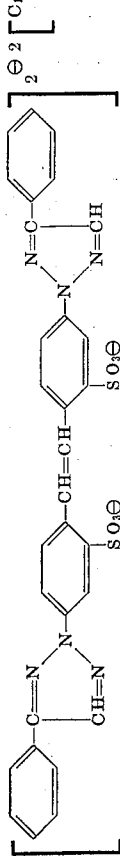
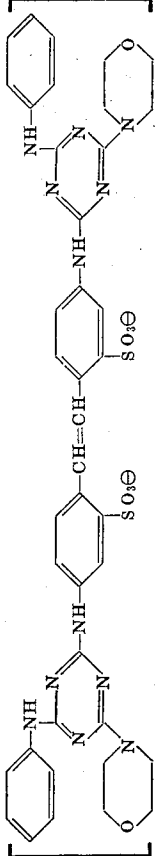
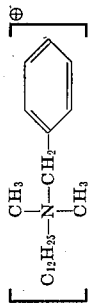
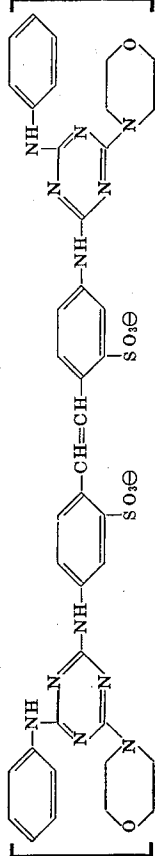
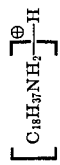
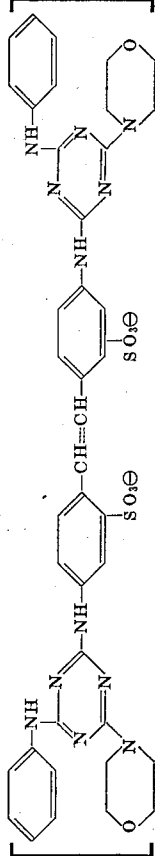
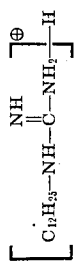
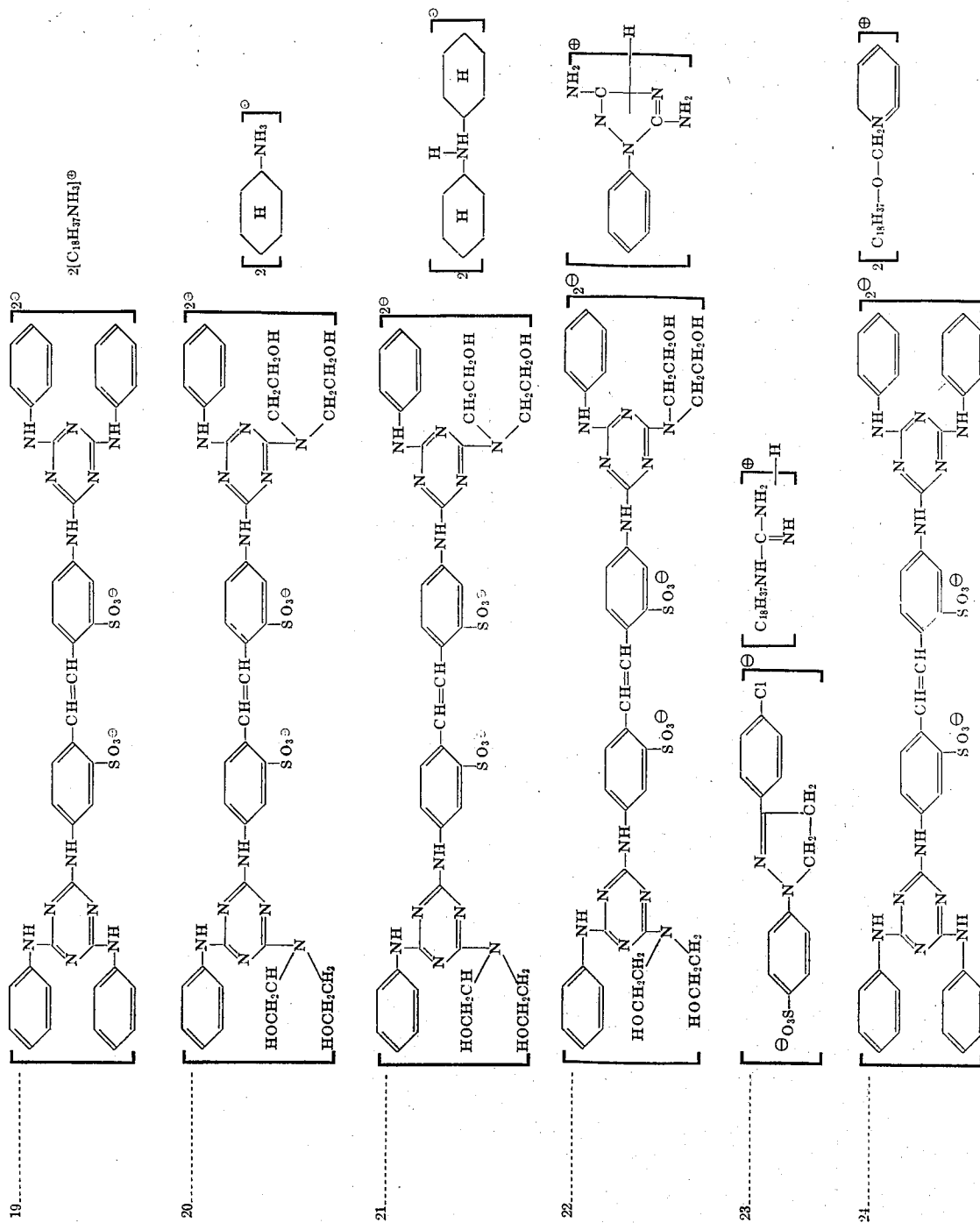


TABLE I - Continued

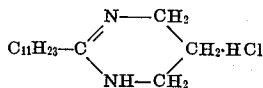
Example number Optical brightener salts



Then 10 g of a bleached cotton fabric are introduced at 45° into the resulting brightener bath, and the fabric is treated in said bath at 45° for 30 minutes with continuous circulation of the brightening liquor. The brightened fabric is then squeezed out and dried in the usual manner. A strong, brilliant white-effect is obtained on said material.

EXAMPLE 32

300 mg of the sodium salt of the optical brightener of the formula given in Example 1 are dissolved in 50 g of methanol. Separately, 150 mg of a compound of the formula



are dissolved in 25 g of methanol. Both solutions are then poured together, stirred well and subsequently diluted with 2,000 g of perchloroethylene. Small amounts of precipitated substances, which mainly consist of sodium chloride, are removed from the solution by filtration. The thus obtained brightener bath is heated to 40° whereupon 100 g of bleached cotton cretonne are introduced into the bath and the textile material is treated in said bath at the same temperature for 45 minutes.

Finally, the brightened cotton cretonne is squeezed out and dried in warm air.

A strong, brilliant white-effect is obtained on the cotton cretonne.

If, in the above Example, instead of 2,000 g of perchloroethylene the same amount of trichloroethylene or dichloroethane is used, similar white-effects are obtained on cotton cretonne.

EXAMPLE 33

25 mg of the optical brightener salt described in Example 2 are dissolved in 0.5 g of dimethylformamide. The resulting solution is then added to 200 g of a solvent mixture consisting of 94 percent by weight of trichloroethylene and 6 percent of methanol. Thereafter, 10 g of cotton poplin are introduced at room temperature into the obtained brightener bath and the textile material is treated in said bath at room temperature for one hour with continuous circulation of the brightening bath.

A level and strong white-effect is obtained.

If, instead of cotton poplin a fabric or a knitted fabric made from Polyamide 6 or Polyamide 6.6 or a fabric made from cellulose-2½-acetate is used, similar brightenings are obtained.

If, in the above Example the 94 percent by weight of trichloroethylene are replaced by the same amount of one of the hydrocarbons given in the following Table II, column 2, the procedure being otherwise as described in the Example, then white-effects of similar quality are obtained.

TABLE II

Ex. No.	Hydrocarbons
34	chlorobenzene
35	1:1 mixture of chlorobenzene and perchloroethylene
36	xylene
37	1:1 mixture of chlorobenzene and xylene
38	trichloroethane
39	1,1,2-trifluoro-2,2,1-trichloroethane

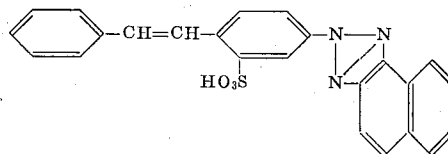
If in Examples 33 to 39 instead of 6 percent by weight of methanol the same amount of one of the solvents given in the following Table III, column 2 is used, the procedure being otherwise as described in the Example, then also level and well developed optical brightenings are obtained.

TABLE III

Ex. No.	Solvents miscible with water
40	ethanol
41	isopropanol
42	ethyleneglycol monomethyl ether
43	tetrahydrofurfuryl alcohol
44	dioxane
45	N-methylpyrrolidone
46	dimethylformamide
47	dimethylacetamide

EXAMPLE 48

215 mg of the stilbyl-naphthatriazole-sulphonic acid of the formula



are dissolved in 50 g of methanol. Separately, 120 mg of 2-undecyl-tetrahydropyrimidine are dissolved in 30 g of methanol and the 2 solutions are combined, whereupon the methanolic solution of the amine salt is formed. The solution is stirred well and then diluted with 2,000 g of perchloroethylene. The resultant brightener bath is heated to 40° whereupon 100 g of bleached cotton cretonne are introduced into the bath and the textile material is treated therein at the same temperature for 45 minutes. Finally, the brightened cotton cretonne is squeezed out and dried in warm air.

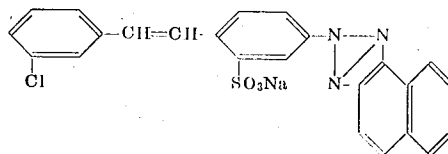
A strong, brilliant white-effect is obtained on cotton cretonne.

If, in the above Example, instead of 2,000 g of perchloroethylene the same amount of trichloroethylene or dichloroethane is used, similar white-effects are obtained on cotton cretonne.

If, in the above Example, instead of cotton cretonne a fabric made from bleached wool is used, the procedure being otherwise as described, a good white-effect is also obtained.

EXAMPLE 49

250 g of the optical brightener salt of the formula



are dissolved in 5 g of dimethylformamide. The resulting solution is added to 2,000 g of a solvent mixture consisting of 95 percent by weight of perchloroethylene and 5 percent by weight of ethanol. 100 g of polyamide-6 fabric are introduced into the resulting clear, fluorescent solution at 60° and the textile mate-

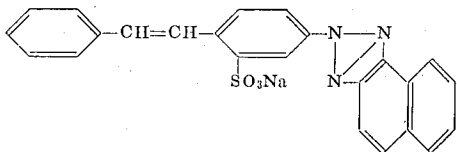
rial is treated for 30 minutes at this temperature, with constant agitation. Thereafter the brightened fabric is squeezed out and dried in warm air.

The polyamide-6 fabric thus treated shows a brilliant uniform white.

If, in the above example, a fabric of polyamide-6,6 or polyamide 12 or a fabric of bleached cotton or bleached wool is used, in place of the polyamide-6 fabric, the procedure otherwise remaining the same, a brilliant white effect is obtained on these materials also.

EXAMPLE 50

30 mg of the optical brightener salt of the formula



are dissolved in 0.5 g of N-methyl-pyrrolidone. The re-

sulting clear solution is added to 150 g of a solvent mixture consisting of 96 percent by weight of perchloroethylene and 4 percent by weight of methanol. Thereafter, the resulting brightener liquor is warmed to 40°, 10 g of polyamide-6 fabric are introduced into the liquor at this temperature, and the textile material is treated at constant temperature for 30 minutes, with constant agitation. Thereafter, the brightened fabric is squeezed out and dried in warm air.

The fabric treated in this way shows a high, brilliant white effect which is fast to water and to dry cleaning.

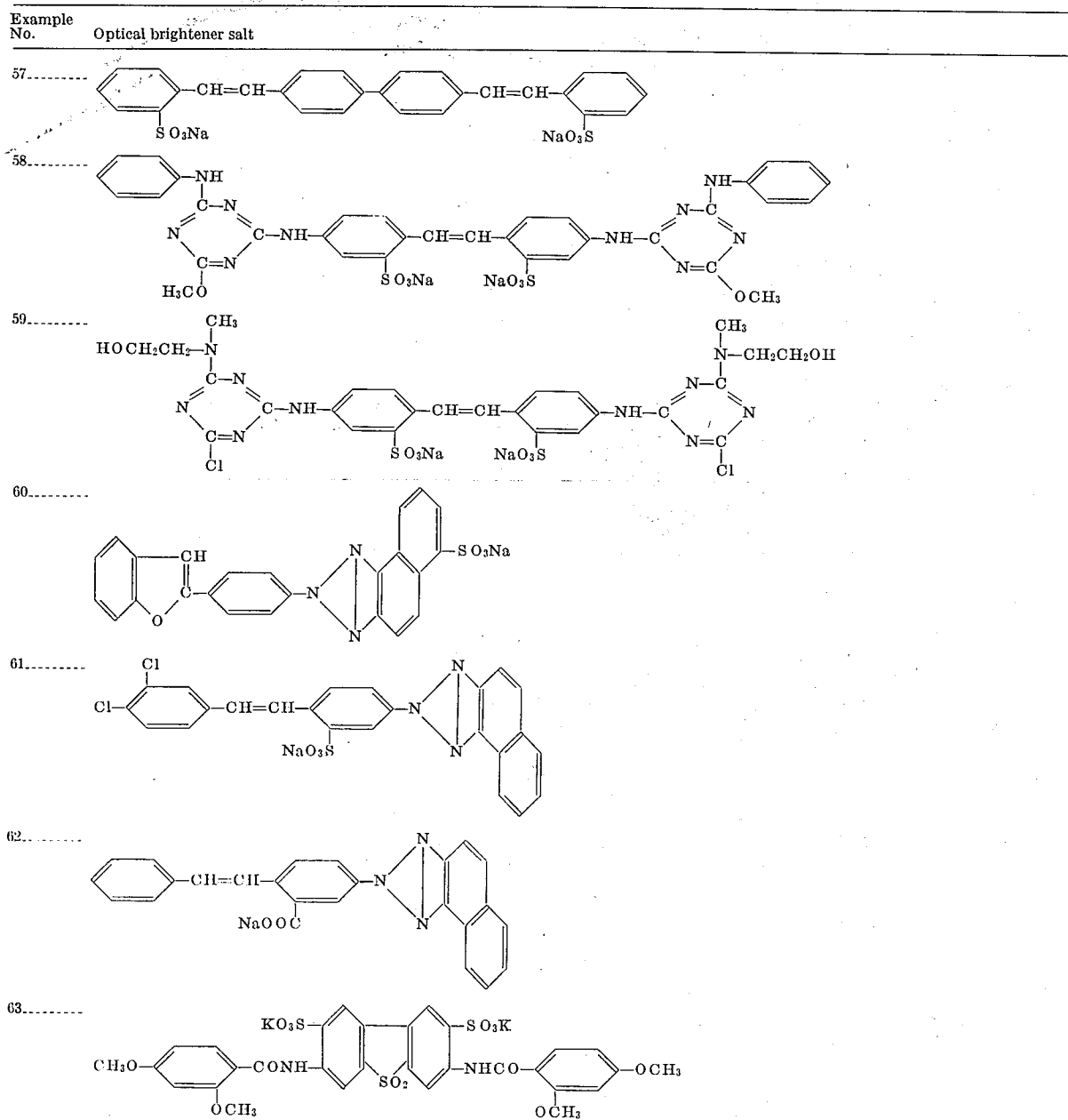
If, in the above example, a fabric of bleached wool or of bleached cotton is used, the procedure otherwise remaining the same, a brilliant, strong white effect is again obtained.

If, instead of the brightener salt indicated in the above example, the same amount of one of the brightener salts listed in Table IV below, column 2, is used, and in other respects the procedure indicated in the example is followed similar brightening effects are obtained on the materials mentioned.

TABLE IV

Example No.	Optical brightener salt
51	
52	
53	
54	
55	
56	

Table IV - Continued



EXAMPLE 64

90 mg of the optical brightener salt described in Example 50 are dissolved in 5 g of N-methylpyrrolidone and 90 mg are dissolved in 5 g of water. The first stock solution is mixed with 800 g (= approx. 500 ml) of a solvent mixture of 97 percent by weight of perchloroethylene and 3 percent by weight of methanol, whilst the aqueous stock solution is diluted with 500 g of water. Both solutions are subsequently halved, and in each of the four solutions obtained 15 g of a polyamide-6 tricot are treated for 45 minutes, one fabric being treated in the organic brightener liquor at 25°, one in the aqueous liquor at 25°, one in the brightener liquor at 40° and one in the aqueous liquor at 40°. Thereafter, the brightened fibre material is squeezed out and dried in a warm stream of air. The brightenings obtained are rated by determining the fluorescence counts with a Harrison fluorimeter.

50 The above experiments are repeated under the same conditions, but using a bleached cotton fabric instead of polyamide-6 tricot.

The ratings with the Harrison fluorimeter give the following results:

Treatment	Fluorescence counts measured with the Harrison fluorimeter*			
	Polyamide-6 25° C	Polyamide-6 40° C	Cotton 25° C	Cotton 40° C
60 aqueous application	122	173	179	178
65 application from solvent mixture	154	182	186	209

* Model EE-100B (manufactured by: Engineering Equipment Co., Boynton Beach, Fla., USA).

The above results show that as a result of the application, according to the invention, from a solvent mixture, substantially better development of the brightener salts on the substrate is achieved as compared to aqueous application.

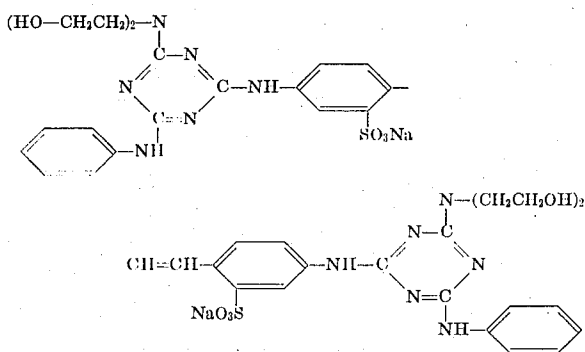
EXAMPLE 65

30 mg of the optical brightener salt described in Example 50 are dissolved in 0.5 g of N-methylpyrrolidone. The resulting clear solution is added to 150 g of a solvent mixture consisting of 94 percent by weight of perchloroethylene and 6 percent by weight of n-butanol. Thereafter, 10 g of a bleached cotton fabric are introduced at 75° C into the brightener liquor obtained, and the fabric is treated for 30 minutes at 75° C whilst constantly circulating the liquor. Thereafter, the brightened fabric is squeezed out and dried in the usual manner.

A level, strong white effect is obtained on the treated cotton fabric.

EXAMPLE 66

30 mg of an optical brightener of the formula



are dissolved in 1.5 ml of methanol. The clear solution obtained is added to 150 g of the solvent mixture given in Example 65 and the procedure of Example 65 is followed.

A uniform, strong white effect is obtained on the treated cotton fabric.

EXAMPLE 67

35 mg of the optical brightener salt described in Example 49 are dissolved in 0.5 g of dimethylformamide. Thereafter, the solution obtained is added to 200 g of a solvent mixture consisting of 97 percent by weight of trichloroethylene and 3 percent by weight of methanol. 10 g of cotton poplin are then introduced into the brightener liquor obtained, at 50°, and the textile material is treated at this temperature for 1 hour, whilst constantly circulating the liquor. After the usual squeezing out and drying, a uniform and strong white effect is obtained.

If, instead of cotton poplin, a woven fabric or knitted fabric of polyamide-6 or polyamide-6,6 is used, similar brightening effects are obtained.

If, in the above example, the 97 parts by weight of trichloroethylene are replaced by an equal amount of one of the hydrocarbons indicated in Table V below, column 2, and in other respects the procedure indicated in the example is followed, brilliant white effects are also obtained.

TABLE V

Ex. No.	Hydrocarbons
5	68 chlorobenzene
	69 xylene
	70 1,1,1-trichloroethane
	71 1,1,2-trichloro-1,2,2-trifluoroethane
	72 carbon tetrachloride
	73 1:1 mixture of chlorobenzene and perchloroethylene
10	74 1:1 mixture of chlorobenzene and trichloroethane

If, in Examples 67 to 74 the same amount of one of the solvents indicated in Table VI below, column 2, is used instead of 3 percent by weight of methanol, and in other respects the procedure given in this example is followed, level and well-developed optical brightenings are also obtained.

TABLE VI

Ex. No.	Water-miscible solvents
25	75 ethanol
	76 isopropanol
	77 n-butanol
	78 ethylene glycol monomethyl ether
	79 ethylene glycol monoethyl ether
	80 tetrahydrofurfuryl alcohol
	81 benzyl alcohol
	82 dioxane
30	83 N-methylpyrrolidone
	84 dimethylformamide
	85 dimethylacetamide
	86 acetonitrile
	87 acetone
	88 glacial acetic acid

We claim:

1. A process for the non-aqueous optical brightening of organic fibre material by the exhaustion method, which essentially comprises the steps of
 - a. treating said fibre material, at a goods: liquor ratio of at least 1:5 in the solution of
 - I. at least one optical brightener salt consisting of the anionic radical of an anionic optical brightener and at least one cationic radical of an inorganic base,
 - II. a solvent mixture consisting of
 - α. from 50 to 99 percent by weight of halogenated hydrocarbon boiling between 50° and 150°C, the balance consisting of
 - β. a liquid, water-soluble organic solvent boiling below 220° C and selected from the group consisting of alkanols, cyloaliphatic alcohols, araliphatic alcohols, aliphatic and cycloaliphatic ketones, alkylene glycol monoalkyl ethers, furfuryl alcohol, tetrahydrofurfuryl alcohol, lower cyclic ethers, lower anhydrous monocarboxylic acids, N,N-dialkylamides of lower monocarboxylic acids, amides of carbonic acid, cyclic amides, lower carboxylic acid nitriles, and mixtures thereof which are soluble in water, at a temperature between room temperature and the boiling point of the solvent mixture, optionally under pressure, and
 - b. finishing the brightened fibre material by removing excess solvent and drying.
2. A process as defined in claim 1, wherein the optical brightener salt defined under (I) is an alkali metal

salt or ammonium salt of an optical brightener containing sulphonic acid groups and/or carboxylic acid groups.

3. A process as defined in claim 1, wherein the anionic optical brightener defined under (I) is selected from derivatives of distyryl acids, 4,4'-bis-triazinylamino-stilbene-sulphonic acids, stilbylnaphthotriazole-carboxylic acids or sulphonic acids, 4,4'-bis-*v*-triazolyl-stilbene-sulphonic acids or of derivatives of diaryl- and triaryl-pyrazolines containing carboxylic acid or sulphonic acid groups.

4. A process as defined in claim 1, wherein the solvent mixture defined under (II) consists of

α . from 80 to 99 percent by weight of halogenated lower aliphatic hydrocarbon having a boiling point between 50° and 150°C, the balance consisting of

β . a liquid, water soluble, organic solvent boiling below 220°C and selected from the group consisting of alkanols, cycloaliphatic alcohols, araliphatic alcohols, aliphatic and cycloaliphatic ketones, alkylene glycol monoalkyl ethers, furfuryl alcohol, tetrahydrofurfuryl alcohol, lower cyclic ethers, lower anhydrous monocarboxylic acids, N,N-dialkylamides of lower monocarboxylic acids, amides of carbonic acid, cyclic amides, lower carbox-

ylic acid nitriles, and mixtures thereof which are soluble in water.

5. A process as defined in claim 1, wherein the solvent mixture defined under (II) consists of

α . from 90 to 99 percent by weight of trichloroethylene, tetrachloroethylene, trichloroethane or trifluorotrichloroethane, the balance consisting of

β . a lower alkanol, an N,N-dialkylamide of a lower monocarboxylic acid, a lower alkylene glycol monoalkyl ether, or a ketone, or mixtures thereof.

6. A process as defined in claim 5, wherein said lower alkanol is methanol or ethanol.

7. A process as defined in claim 5, wherein said N,N-dialkylamide of a lower monocarboxylic acid is dimethylformamide or dimethylacetamide.

8. A process as defined in claim 5, wherein said lower alkylene glycol monoalkyl ether is ethylene monoglycol methyl ether.

9. A process as defined in claim 5, wherein said ketone is acetone.

10. A process as defined in claim 1, wherein said organic fibre material consists of cellulose fibres, natural or synthetic polyamide fibres.

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