United States Patent Office 2,980,549 Patented Apr. 18, 1961

2,980,549

BRIGHTENING OF FINE FABRICS

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No Drawing. Filed June 21, 1956, Ser. No. 592,721

7 Claims. (Cl. 117—33.5)

This invention relates to the treatment of textile materials such as fibers, filaments and fabrics for the purpose of brightening the same. More particularly, this invention relates to a novel process for brightening textile materials involving the use of diphenylindoles as brightening agents.

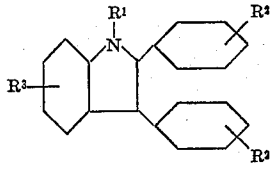
White and dyed textile fibers, filaments and fabrics of synthetic materials are often treated with compounds, hereinafter called brightening agents, which whiten and brighten the white textile products and brighten the colors of the dyed textile products. It is an important object of this invention to provide an improved process for treating textile materials to whiten and brighten the same.

Another object of this invention is the provision of an improved process for brightening textile materials by treating the same with an aqueous dispersion of a diphenylindole.

A further object of this invention is the provision of novel brightening agents comprising substituted diphenylindoles.

Other objects of this invention will appear from the following detailed description and claims.

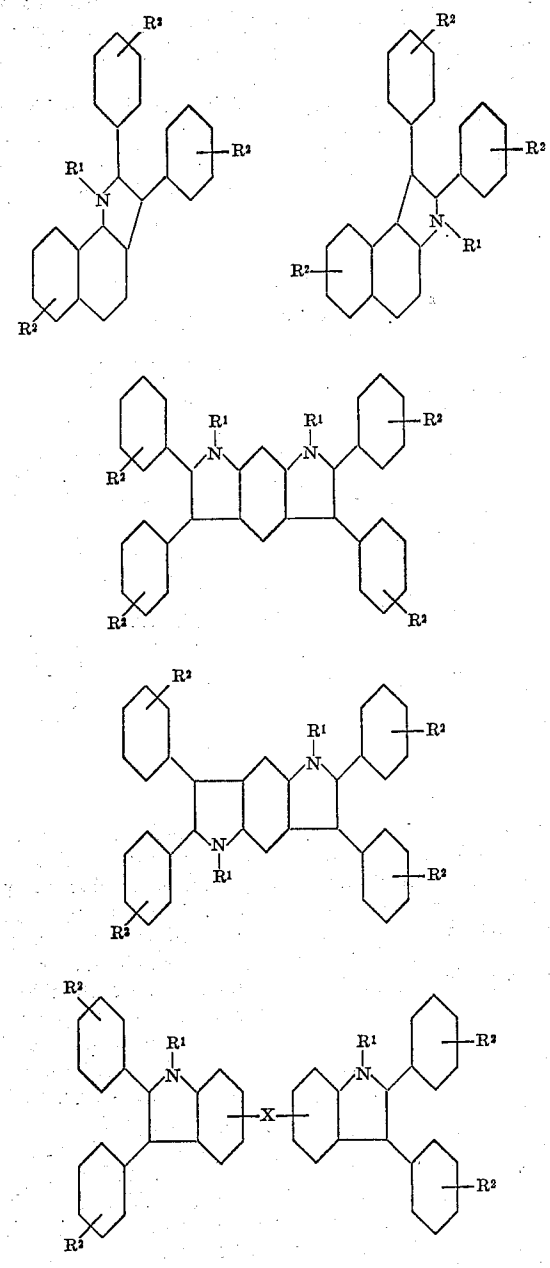
In accordance with this invention, the brightening of textile fibers, filaments and fabrics of synthetic materials is effected by applying to said fibers, filaments and fabrics compounds consisting of diphenylindoles and of variously substituted diphenylindoles such as, for example, 2,3-diphenylindoles which are represented by the following formula:



where R^1 may be hydrogen, alkyl, aryl, arylalkyl, alicyclic, or an alkyl group containing atoms other than carbon, such as oxygen, nitrogen, and the like, as exemplified by β-hydroxyethyl, β-aminoethyl, β-cyanoethyl, etc., and R^2 and R^3 may be hydrogen, alkyl, aryl, arylalkyl, or any non-chromophoric group such as hydroxyl, alkoxyl, amino,

alkylamino, acylamido, carboalkoxyl, cyano, and the like. R^2 and R^3 may also be halogen. More than one R^3 may be present on the benzenoid ring of the indole nucleus.

Related compounds which are also useful for brightening textile materials can be represented by the following formulas:



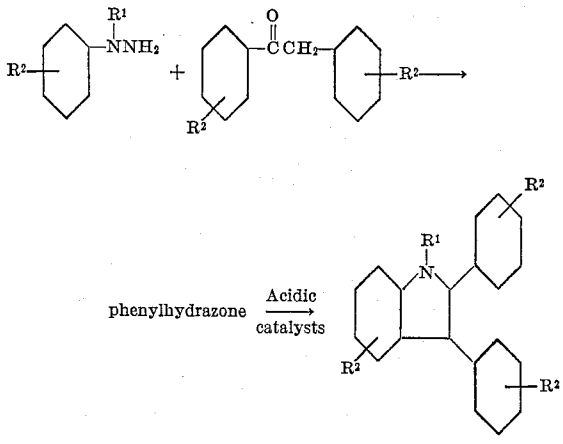
where R^1 and R^2 are defined as above and X is $—CH_2—$;

—O—, —S—, —SO_2—, —CO—, a diphenyl linkage, and the like.

The aforementioned compounds are suitable in some cases for use in brightening textile materials of nylon, cellulose esters, a polyester of terephthalic acid and ethylene glycol, a polymer of acrylonitrile, a copolymer of acrylonitrile and vinyl chloride.

Preferably, the brightening agents of this invention are applied to the textile materials from an aqueous dispersion. Thus, the diphenylindole to be used is dissolved in a suitable water-miscible organic solvent such as, for example, ethyl alcohol, acetone, dimethylformamide, dioxane, or a mixture of two of said solvents, and a small amount of the solution is added to water whereby a milky dispersion is obtained. The textile materials are treated with this dispersion. It has been found that the presence of soap or a synthetic surface active agent in said dispersion is beneficial. Satisfactory brightening of textile materials may also be obtained by washing the same, employing ordinary washing operations, with a soap or a synthetic detergent in which the diphenylindoles are incorporated. Also these compounds may be applied in the form of the amine acid salt.

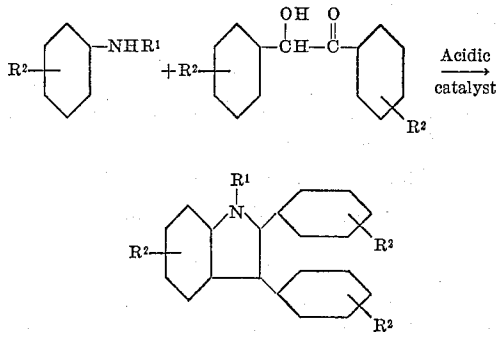
The diphenylindoles employed in accordance with the instant invention may be prepared from the appropriate phenylhydrazine and the appropriate α-phenylacetophenone by the Fischer indole synthesis, as follows:



The phenylhydrazines might be chosen from the following: p-amino-, m-amino-, p-acetamido-, m-acetamido-, p-formamido-, m-formamido-, p-chloro-, m-chloro-, p-bromo-, m-bromo-, 2,4-dichloro-, 2,4-dibromo-, p-phenyl-, o-phenyl-, p-methoxy-, o-methoxy-, p-ethoxy-, p-hydroxy-, m-hydroxy-, o-methyl-, m-methyl-, p-methyl-, 2,5-dimethyl-, 2,3 - dimethyl-, 2,5 - dimethoxy-, 4 - acetamido-2-methyl-, p-carbethoxy-, and the like. α- and β-naphthylhydrazines and substituted naphthylhydrazines such as 4-bromo-, 4-chloro-, 5-methoxy-, 5-acetamino-, and 8-acetamido - α - naphthylhydrazine and 3 - bromo-, 3-chloro-, 5-methoxy-, 6-methoxy-, 3-acetamido-, 6-acetamido- and 7-acetamido-β-naphthylhydrazine can also be used. The dihydrazines prepared by diazotization and reduction of 4,4'-biphenyldiamine (benzidine), 2,4'-biphenyldiamine, di(p-aminophenyl) methane, and di(o-aminophenyl)methane may also be used.

The α-phenylacetophenones may be selected from the following substituted acetophenones: α-(p-aminophenyl)-, p-amino-α-(p-aminophenyl)-, α-(m-aminophenyl)-, α-(p-acetamidophenyl)-, α-(p-methoxyphenyl)-, α-4-biphenyl-yl-, p-bromo-α-(p-bromophenyl)-, o-bromo-α-phenyl, p-chloro-α-phenyl, α-(o-chlorophenyl)-, 2,4-dihydroxy-α-phenyl-, α-(2,4-dimethoxyphenyl)-, α-(2,3-dimethoxyphenyl)-2,3-dimethoxy-, 3-hydroxy-α-(p-hydroxyphenyl)-, p-methoxy-α-phenyl-, α-(m-methoxyphenyl)-, and α-(p-methoxyphenyl)acetophenone.

Alternatively, the diphenylindoles may be prepared by condensation of the appropriate aromatic amine with the appropriate benzoin, as follows:



Some of the amines which may be used as o-, m-, and p-toluidine; o-, m-, and p-anisidine; m- and p-chloro and bromo anilines; m- and p-aminoacetanilides; 2- and 4-biphenylamine; N-methyl-, N-ethyl, N-(β-hydroxyethyl)-, and N-benzyl-anilines; N-methyl-, o-, m- and p-toluidines; the xylidines; 2,5-dimethoxyaniline; o-, m- and p-aminophenol; m- and p-amino-N-methylacetanilides; α- and β-naphthylamine; 3-chloro-, 5-methoxy-, 4-acetamido-, 5-acetamido- and 8-acetamido-α-naphthylamine; 3-bromo-, 3-chloro-, 3-acetamido-, 6-acetamido-, 3-hydroxy-, and 6-hydroxy-β-naphthylamine. The bis-2,3-diphenylindoles can be prepared from 4,4'-biphenyldiamine, 2,4'-biphenyldiamine, di(p-aminophenyl)methane, di(o-aminophenyl)methane, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminobenzophenone, and the like.

Benzoin or substituted benzoins such as 4-methoxy-, 3,4-methylene-dioxy-, 4-dimethylamino-, 2-hydroxy-, 2'-hydroxy-, 4'-methoxy-, 2,2'-dimethoxy-, 4,4'-dimethoxy-, 4,4' - diacetamino-, 3,3',4,4',5,5'-hexamethoxy, 4,4'-diphenyl, 4-phenyl-, 4-chloro-, 4'-chloro-, 4,4'-dichloro-, 3,3'-dichloro-, 4-chloro-4'-methoxy-, 4,4'-diaminobenzoin, and the like, may be used.

Groups may also be introduced into the parent 2,3-diphenylindole by substitution reactions; for example, the hydrogen on the nitrogen of the indole ring can be replaced by alkyl groups by alkylation, as for example, with alkyl halides (e.g., methyl iodide, ethyl iodide), alkyl sulfates (dimethyl and diethylsulfate). The β-cyanoethyl group may be introduced by cyanoethylation with acrylonitrile in the usual manner. Nitration followed by reduction gives the amino-substituted 2,3-diphenylindole which may be converted to acyl derivatives.

The amount of the 2,3-diphenylindole employed in treating the textile material is from 0.05 to 0.5%, based on the weight of the textile material.

Appreciable brightening of the colors is also observed when the compounds employed in the instant invention are incorporated in films and plastic bodies having a basis of the synthetic materials of the fibers, filaments and fabrics above mentioned.

The instant invention is further illustrated by the

following examples which are not intended to be in any way limitative.

Example I

To a jar containing 64 ml. of water, 25 ml. of a solution of Glauber's salt (solution contained 20 mg. of $Na_2SO_4.10H_2O$ per ml. of solution) and 10 ml. of dilute formic acid (solution contained 12.5 mg. of formic acid per ml. of solution) at about 180° F. was added 1 ml. of an alcohol solution containing 125 mg. of 2,3-diphenylindole per 50 ml. of solution. A 5 g. swatch of nylon was placed in the jar, the jar capped, and agitation at about 180° F. was carried out for 20 minutes. The swatch was removed, rinsed well, and dried. This swatch was compared with another which was given the same treatment without the addition of the 2,3-diphenylindole. The fabric which had been treated with the 2,3-diphenylindole was noticeably whiter in daylight.

Example II

The procedure of Example I was repeated except that 55 ml. of water and 10 ml. of the solution of the 2,3-diphenylindole were used. The resulting fabric was markedly whiter than the blank.

Example III

The procedure of Example I was repeated using a ¼% alcohol-acetone solution of 6-methyl-2,3-diphenylindole with the same results.

Example IV

The procedure of Example I was repeated using an alcohol-acetone solution of 5-methoxy-2,3-diphenylindole disclosed and claimed in Patent No. 2,845,437 with the same results.

Example V

The procedure of Example I was repeated using an alcohol-acetone solution of 1,2-diphenyl-3H-benz(e)-indole with the same results.

Example VI

The procedure of Example I was repeated using a ¼% acetone-dimethyl-formamide solution of 6-acetamido-2,3-diphenylindole disclosed and claimed in copending application Ser. No. 592,746, filed on even date herewith, now abandoned, with the same results.

Example VII

The procedure of Example I was repeated using an acetone-dimethyl-formamide solution of 5,5'-bis-2,3-diphenylindole with the same results.

Example VIII

The procedure of Example II was repeated with 6-methyl-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example IX

The procedure of Example II was repeated with 5-methoxy-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example X

The procedure of Example II was repeated with 1,2-diphenyl-3H-benz(e)indole and the resulting fabric was markedly whiter in daylight.

Example XI

The procedure of Example II was repeated with 6-acetamido-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example XII

The procedure of Example II was repeated with 5,5'-bis-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example XIII

The procedure of Example I was repeated with a 5 g. swatch of cellulose acetate being used in place of nylon. Noticeable whitening in daylight was observed.

Example XIV

The procedure of Example XIII was repeated with 6-methyl-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example XV

The procedure of Example XIII was repeated with 5-methoxy-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example XVI

The procedure of Example XIII was repeated with 1,2-diphenyl-3H-benz(e)indole and the resulting fabric was markedly whiter in daylight.

Example XVII

The procedure of Example XIII was repeated with 6-acetamido-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example XVIII

The procedure of Example XIII was repeated with 5,5'-bis-2,3-diphenylindole and the resulting fabric was markedly whiter in daylight.

Example XIX

The procedure of Example II was repeated with a 5 g. swatch of cellulose acetate being used in place of nylon. Noticeable whitening was observed.

Example XX

The procedure of Example XIX was repeated with 6-methyl-2,3-diphenylindole and the resulting fabric was markedly whiter.

Example XXI

The procedure of Example XIX was repeated with 5-methoxy-2,3-diphenylindole and the resulting fabric was markedly whiter.

Example XXII

The procedure of Example XIX was repeated with 1,2-diphenyl-3H-benz(e)indole and the resulting fabric was markedly whiter.

Example XXIII

The procedure of Example XIX was repeated with 6-acetamido-2,3-diphenylindole and the resulting fabric was markedly whiter.

Example XXIV

The procedure of Example XIX was repeated with 5,5'-bis-2,3-diphenylindole and the resulting fabric was markedly whiter.

Example XXV

To 200 ml. of water containing 0.4 g. of soap at about 150° F. was added with agitation a 5 ml. aliquot of an acetone-alcohol solution containing 125 mg. of 6-methyl-2,3-diphenylindole per 50 ml. of solution. A 5 g. swatch of nylon was added and the system agitated at about 150° F. for 20 minutes. The cloth was rinsed well and agitated with soap solution containing no brightener at 150° F., again rinsed well and dried. Another swatch of cloth was treated similarly except that no brightener was added. Comparison of the two swatches showed that considerable whitening in daylight was imparted by the indole to the treated swatch.

Example XXVI

The procedure of Example XXV was repeated with a synthetic detergent (Tide) and cellulose acetate. Whitening in daylight was observed.

Example XXVII

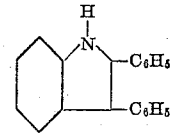
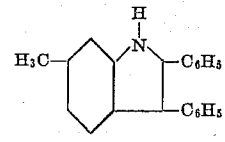
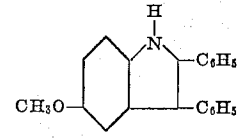
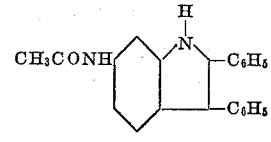
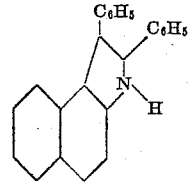
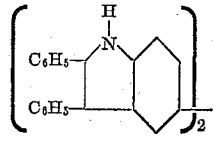
The procedure of Example II was repeated with a 5 g. swatch of Dacron and with 6-acetamido-2,3-diphenylindole. A noticeable whitening in daylight resulted.

Example XXVIII

The procedure of Example XXVII was repeated with 5,5'-bis-2,3-diphenylindole. A noticeable whitening was observed.

The following tables set out instrument readings made on the swatches of fabric treated in accordance with the procedures of the above examples, along with those made on blanks.

TABLE 1

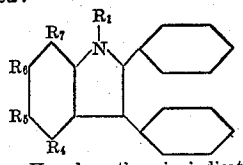
Compound	Brightener Concentration in Batch (percent by wt. of cloth)	Nylon		Cellulose Acetate	
		R [1]	B [2]	R	B
Blank (untreated fabric)		49	3	43	2
	0.5	28	60	28	44
	0.05	43	26	41	13
	0.5	24	75	27	61
	0.05	42	31	37	20
	0.5	29	52	27	41
	0.05	44	21	40	13
	0.5	30	56	24	49
	0.05	38	37	38	19
	0.5	27	17	29	11
	0.5	40	19	36	16

[1] R=Reflectance.
[2] B=Brightness.

TABLE 2

[Table 2 describes brightness values of many other compounds which were tested. The dyeings are at a concentration of .000005 mole of brightener per gram of cloth.]

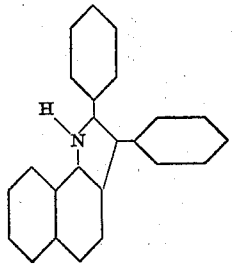
Compound tested:



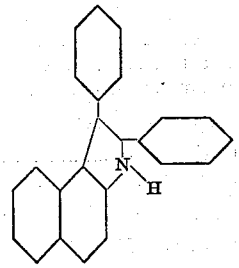
[R=—H, unless otherwise indicated]

R_1	R_4	R_5	R_6	R_7	Nylon	Cellulose Acetate
					18	30
$-CH_3$					+	13-14
			$-CH_3$		30	35
		$-C_6H_5$			16	25
		$-Cl$			11	11
		$-OCH_3$			30	35
		$-NHCOCH_3$			16	25
$-C_2H_5$					+	+
		$-CH_3$			18	30
				$-CH_3$	11	11
$-CH_3$		$-CH_3$			+	10
$-C_6H_5$					+	<10
				$-C_6H_5$	+	10-11
			$-Cl$		25	25
				$-OCH_3$	10	10
			$-NHCOCH_3$		40	45
		$-CH_3$	$-CH_3$		15	15
		$-CH_3$		$-CH_3$	15	15
	$-CH_3$			$-CH_3$	10-11	10-11
	$-OCH_3$			$-OCH_3$	10-11	13-14
			$-\overset{CH_3}{\underset{|}{N}}COCH_3$		10-11	10-11

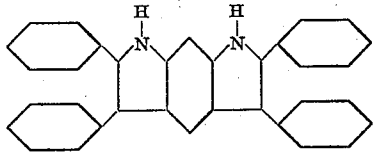
Compound Tested



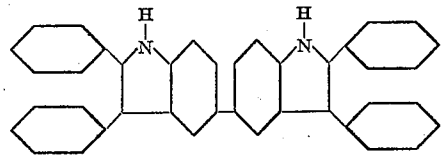
16 17



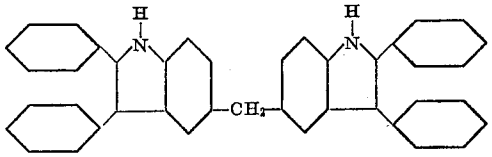
19 20



16 28



16 28



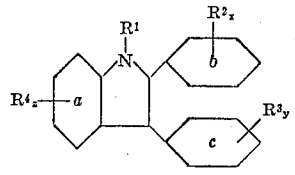
10-11 12-13

The + signs mean that a slight fluorescence on the fabrics over untreated fabric could be observed but too little for any brightness reading, probably less than 5.

It is to be understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of my invention.

Having described my invention, what I desire to secure by Letters Patent is:

1. Process for achieving a brightening effect on white and colored fibers, filaments and fabrics of synthetic materials, which comprises applying to said fibers, filaments and fabrics an aqueous dispersion of from 0.05 to 0.5%, based on the weight of said fibers, filaments and fabrics, in a water-miscible organic solvent therefor, of a diphenylindole of the formula



wherein R^1 represents a member of the class consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl, hydroxyalkyl, cyanoalkyl, aminoalkyl, and mono- and di-alkyl substituted aminoalkyl; R^2, R^3 and R^4 represent members of the class consisting of hydrogen, alkyl, alkoxy, hydroxy, carbalkoxy, cyano, amino, mono- and di-alkylamino, acylamido, aryl and aralkyl; R^4 may additionally represent a second identical indole moiety connected by a connecting linkage which is a member of the class consisting of CH_2, O, S, SO_2, CO, CONH and a diphenyl linkage; *x*, *y* and *z* represent one of the integers 1–3; and wherein the ring designated *a* may be fused to a benzene ring and a pyrrole ring which is further substituted by diphenyl rings as defined by the rings designated *b* and *c*.

2. Process for achieving a brightening effect on white and colored fibers, filaments and fabrics of synthetic materials, which comprises applying to said fibers, filaments and fabrics an aqueous dispersion of from 0.05 to 0.5%, based on the weight of said fibers, filaments and fabrics, in a water-miscible organic solvent therefor, of 2,3-diphenylindole.

3. Process for achieving a brightening effect on white and colored fibers, filaments and fabrics of synthetic materials, which comprises applying to said fibers, filaments and fabrics an aqueous dispersion of from 0.05 to 0.5%, based on the weight of said fibers, filaments and fabrics, in a water-miscible organic solvent therefor, of 2,3-diphenylindole substituted in at least one of the phenyl groups by a member of the class consisting of alkyl, alkoxy, hydroxy, carbalkoxy, cyano, amino, mono- and di-alkylamino, acylamido, aryl and aralkyl.

4. Process for achieving a brightening effect on white and colored fibers, filaments and fabrics of synthetic materials, which comprises applying to said fibers, filaments and fabrics, at a temperature of from 150 to 180° F., an aqueous dispersion of from 0.05 to 0.5%, based on the weight of said fibers, filaments and fabrics, in a water-miscible organic solvent therefor, of 2,3-diphenylindole.

5. Process for achieving a brightening effect on white and colored fibers, filaments and fabrics of synthetic materials, which comprises applying to said fibers, filaments and fabrics, at a temperature of from 150 to 180° F., an aqueous dispersion of from 0.05 to 0.5%, based on the weight of said fibers, filaments and fabrics, in a water-miscible organic solvent therefor, of 2,3-diphenylindole substituted in at least one of the phenyl groups by a member of the class consisting of alkyl, alkoxy, hydroxy, carbalkoxy, cyano, amino, mono- and di-alkylamino, acylamido, aryl and aralkyl.

6. Process for achieving a brightening effect on white and colored fibers, filaments and fabrics of synthetic materials selected from the group consisting of nylon and cellulose acetate, which comprises applying to said fibers, filaments and fabrics, at a temperature of from 150 to 180° F., an aqueous dispersion of from 0.05 to 0.5%, based on the weight of said fibers, filaments and fabrics, in a water-miscible organic solvent therefor, of 2,3-diphenylindole.

7. Process for achieving a brightening effect on white and colored fibers, filaments and fabrics of synthetic materials selected from the group consisting of nylon and cellulose acetate, which comprises applying to said fibers, filaments and fabrics, at a temperature of from 150 to 180° F., an aqueous dispersion of from 0.05 to 0.5%, based on the weight of said fibers, filaments and fabrics, in a water-miscible organic solvent therefor, of 2,3-diphenylindole substituted in at least one of the phenyl groups by a member of the class consisting of alkyl, alkoxy, hydroxy, carbalkoxy, cyano, amino, mono- and di-alkylamino, acylamido, aryl and aralkyl.

References Cited in the file of this patent

UNITED STATES PATENTS

1,780,058	Ballauf	Oct. 28, 1930
2,057,948	Herdieckerhoff et al.	Oct. 20, 1936
2,460,745	Grimmel et al.	Feb. 1, 1949
2,510,428	Standen	June 6, 1950
2,510,432	Stewart	June 6, 1950
2,713,046	Williams et al.	July 12, 1955

FOREIGN PATENTS

112,132	Austria	Jan. 25, 1929
533,471	Germany	Sept. 12, 1931

OTHER REFERENCES

Chemical Abstracts, vol. 33 (1939), page 4127, article by Fialkovskaya.