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2,842,501

OPTICAL BLEACHING COMPOSITIONS

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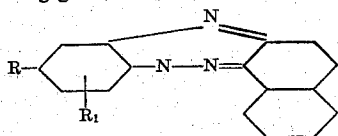
6 Claims. (Cl. 252-117)

This invention relates to new compositions for improving the whiteness of synthetic fibrous materials and to the method of whitening such materials with said treated compositions.

It is well known that textiles tend to develop a yellowish shade on aging which cannot be removed by ordinary bleaching or washing. The prior methods of "bluing" white materials with blue pigments or fugitive blue dyes has largely been superseded in modern practice of laundering by addition of a fluorescent optical bleaching agent (brightener) with the soap or detergent in the washing bath. The brightening agent is conveniently supplied commercially in the form of an intimate admixture with detergent or soap in bars, flakes, powders etc. The fluorescent optical bleaching agents by absorbing ultraviolet radiations and emitting light within the visible range, tend to neutralize any yellowness of the material and thus increase the apparent whiteness thereof.

Numerous organic compounds have been suggested as whiteners or fluorescent brightening agents, such as, for example, stilbenes, dibenzothiophenedioxides, dibenzimidazoleethylenes, dibenzoxazoleethylenes, dibenzthiazoleethylenes, coumarins, benzidines, phenylenediamines, polyarylimidazolones, diarylpyrazolines, triazole derivatives of diamino stilbene disulfonic acids as disclosed in U. S. Patent 2,668,777 and optical bleaching agents containing 1:2:3-triazole rings as disclosed in U. S. Patent 2,666,062, and the like are well known. Such compounds are complex, requiring costly synthesis and are high priced. In addition, such compounds contain sulfonic acid groups, usually two, and as a result are not particularly substantive to fabrics made from synthetic fibers, particularly derivatives of cellulose and superpolyamides (nylons) and are of limited utility for whitening such synthetic fibers.

We have now found that relatively inexpensive brightening compositions for fibrous materials having a basis of superpolyamides (nylon) and of organic derivatives of cellulose are readily obtained by utilizing such compositions containing compounds having only a single 1:2:3-triazole ring. This finding makes it possible to avoid complicated and expensive synthesis, and makes available an inexpensive brightening agent which is very specific for whitening fibrous materials of the aforementioned two classes, and especially nylon. The compounds utilized in accordance with our invention are characterized by the following general formula:



wherein R represents either an amino, N,N-dialkylamino, e. g. N,N-dimethylamino, N,N-diethylamino, N,N-dipropylamino, etc., N,N-bis-β-cyanoethylamino or N-morpholino radical, and R₁ represents either hydrogen, alkyl, e. g. methyl, ethyl, propyl, butyl, etc., alkoxy,

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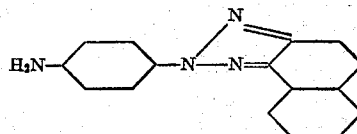
e. g. methoxy, ethoxy, propoxy, etc., and halogen, e. g. bromine or chlorine.

The compounds characterized by the foregoing general formula, which may be referred to as substituted and unsubstituted [naphtho(1,2)triazolyl(2)] anilines and 2-(N-morpholinylphenyl)naphtho(1,2)triazoles, and are readily prepared by refluxing the azo dye obtained by coupling a diazotized substituted or unsubstituted 4-nitro aniline or N-4-aminophenylmorpholine with a substituted or unsubstituted 2-naphthylamine in the usual manner with water, pyridine and aqueous solution of cupric sulfate to yield the nitro-triazole derivative which is then reduced with hydrogen in the presence of Raney nickel catalyst. Further details, including purification of the final product, will become apparent from the working examples. The diazotizable amine, in addition to N-4-aminophenylmorpholine, may be substituted or unsubstituted 4-nitroanilines, such as, for example, 4-nitro-aniline, 2-chloro-4-nitroaniline, 4-nitro-2-toluidine, 4-nitro-2-anisidine, 4-aminodimethyl aniline, N,N-bis(β-cyanoethyl)4-aminoaniline, etc.

As couplers for the diazotized component any substituted or unsubstituted naphthylamine may be employed. However, we prefer to employ 2-naphthylamine.

The following examples will illustrate the manner in which compounds of the above general formula may be readily prepared. All parts are by weight unless otherwise noted.

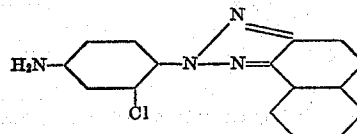
EXAMPLE I



4-[naphtho(1,2)triazolyl(2)]aniline

29.2 parts of the azo dye obtained by coupling diazotized 4-nitroaniline with 2-naphthylamine in the usual manner, 400 parts pyridine, 50 parts by volume concentrated (28%) ammonia and a solution of 50 parts cupric sulfate (CuSO₄·5H₂O) and 300 parts water were refluxed for twelve hours. The precipitated product was filtered and washed with water. The wet cake was slurried with 300 parts water and acidified to pH 2-3 by the addition of 50% sulfuric acid. The mixture was stirred one-half hour, filtered, washed neutral and dried in a vacuum oven at 75° C. 27.7 parts of the obtained nitro-triazole derivative was reduced with hydrogen in 300 grams methanol in the presence of Raney nickel catalyst. After the reduction was completed the product and nickel catalyst were filtered. The product was dissolved in 175 parts hot dioxane and separated from the nickel catalyst by filtration. The amino triazole was precipitated by the addition of 200 parts of water and the product was filtered and dried in a vacuum oven at 75° C. The yield obtained was 21.7 parts of the final product.

EXAMPLE II



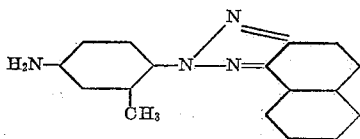
3-chloro-4-[naphtho(1,2)triazolyl(2)]aniline

25.7 parts of the azo dye obtained by coupling diazotized 2-chloro-4-nitroaniline with 2-naphthylamine, 410 parts pyridine and a solution of 50 parts cupric sulfate (CuSO₄·5H₂O) and 250 parts water were heated to 90-95° C. for 6 hours and then cooled to room temperature. The nitro-triazole was filtered, washed with water

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and dried in a vacuum oven at 75° C. 24.4 parts of the chloro nitro-triazole derivative was obtained and this was reduced with hydrogen in methanol in the presence of Raney nickel catalyst as in Example I.

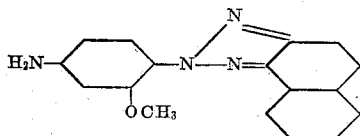
EXAMPLE III



3-methyl-4-[naphtho(1,2)triazolyl(2)]aniline

30.6 parts of the azo dye obtained by coupling diazotized 4-nitro-2-toluidine with 2-naphthylamine, 350 parts pyridine, and a solution of 70 parts cupric sulfate and 350 parts water were heated to 90°-95° C. for six hours or until the color of the azo dye disappeared. The reaction mixture was cooled to room temperature, filtered, washed with water and after drying in a vacuum oven at 75° C., 27.1 parts of the nitro triazole derivative was obtained. The nitro compound was reduced with hydrogen as in Example I.

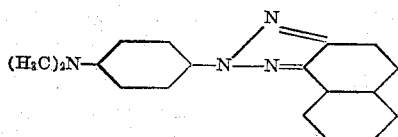
EXAMPLE IV



3-methoxy-4-[naphtho(1,2)triazolyl(2)]aniline

27.6 parts of the azo dye obtained by coupling diazotized 4-nitro-2-anisidine with 2-naphthylamine, 250 parts pyridine, and a solution of 50 parts cupric sulfate and 250 parts water were heated to 90°-95° C. for six hours after which time the oxidation to the triazole was complete. Upon cooling the reaction mixture, the product was filtered, washed with water and dried in a vacuum oven at 75° C., 29.2 parts of the nitro triazole was obtained, which was reduced with hydrogen as in Example I.

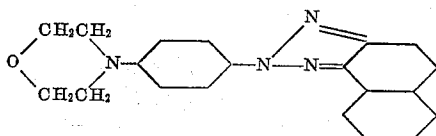
EXAMPLE V



N,N-dimethyl-4-[naphtho(1,2)triazolyl(2)]aniline

29.0 parts of the azo dye obtained by coupling diazotized 4-amino-dimethyl aniline with 2-naphthylamine, 400 parts pyridine and 50 parts cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) dissolved in 200 parts water were heated to 90°-95° C. for four hours until the oxidation to the triazole was complete. The reaction mixture was diluted with 2000 parts water, stirred for one-half hour, filtered, washed with water and dried in a vacuum oven at 75° C., 18.3 parts of product were obtained.

EXAMPLE VI



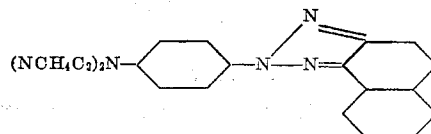
2-(N-morpholinylphenyl)-naphtho(1,2) triazole

116 parts of the azo dye obtained by coupling diazotized N-4-aminophenylmorpholine with 2-naphthylamine, 800 parts pyridine and 195 parts cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) dissolved in 200 parts of water when refluxed for six hours. Upon cooling the reaction mixture was diluted with 3000 parts water, filtered, washed with water and

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dried in a vacuum oven at 75° C., to yield 74.7 parts of the final product.

EXAMPLE VII



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N,N-bis-β-cyanoethyl-4-[naphtho(1,2)triazolyl(2)]aniline

36.8 parts of the azo dye obtained by coupling diazotized N,N-bis(β-cyanoethyl)4-aminoaniline with 2-naphthylamine, 300 parts pyridine and 50 parts cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) dissolved in 300 parts water were heated 90°-95° C. for 5 hours, filtered at room temperature, washed with water and dried in vacuum oven at 75° C., to yield 31 parts of the final product.

In preparing the working compositions in accordance with the present invention we employ any one of the foregoing triazoles or mixtures thereof dissolved in a water miscible organic solvent, for example, lower alcohols, e. g. methanol, ethanol, isopropanol and the like, acetone, dioxane and the like. The amount of such solvent or solvent mixture may vary with the solubility of the brightening agent or mixture of all agents. Such solutions preferably contain from 0.5 to 20% by weight of the brightening agent or mixture. The solution thus prepared is added with agitation to hot water containing a small amount, usually from 0.1 to 5% by weight of a dispersing agent, which is preferably a common soap or soap powder or a synthetic detergent of either the anionic, non-anionic or cationic type. All of these synthetic detergents are well known to those skilled in the art, and reference to their preparation need not be disclosed herein. It is to be noted that the nature or character of either the ordinary soap or soap powder, anionic, non-anionic or cationic detergent is immaterial so long as it functions as a dispersing agent for the brightening compounds.

In employing the solutions prepared as above, we have found that usually one-half ounce by volume of brightening solution may be added to about 3 to 5 gallons of hot water. The fabric to be brightened is placed in the hot water, agitated for a few minutes, rinsed in warm water and then dried. This operation is conveniently carried out during the regular laundering. The solution of brightening agent or mixtures thereof, which may be bottled in solution form, or packaged in dry form for use, is added to the hot water containing soap or synthetic detergent during regular laundering operations.

Such solutions or powders are especially suitable for whitening fine fabrics containing or consisting of nylon and derivatives of cellulose. Within the latter term is included textile materials in the form of filaments, threads, yarn, woven or knitted fabrics, made of cellulose esters such as cellulose acetate, cellulose propionate, cellulose butyrate, and mixed cellulose esters, for instance, cellulose acetate-butyrate and cellulose acetate-propionate, or cellulose ethers such as ethyl cellulose and benzyl cellulose. Also included are synthetic fibrous materials made of any one of the foregoing types of cellulose derivatives not in textile form, e. g. compacted synthetic fibers.

A preferred embodiment of the present invention involves the distribution of the brightening agent or mixture thereof in soap, soap detergent, or synthetic detergent. Thus, for example, solutions of the brightening agents or mixtures thereof, prepared in accordance with Examples I to VII inclusive, are added to aqueous solutions or slurries of soap, soap detergent or synthetic detergent, preferably during their manufacture, or isolated in the usual way, such as, for example, by spray drying. The soap or synthetic detergent containing the brightening agent or mixture thereof is used in the usual laundering procedure, or may be added to a hot water

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bath through which the fabrics can be run during manufacture and processing. The following examples describe the preparation of the brightening compositions and the treatment of fabrics therewith. It is to be understood that these examples are merely inserted for the purpose of illustration, and are not to be construed as limited the scope of the invention claimed. All parts given are by weight unless otherwise specified.

EXAMPLE VIII

About 0.5 part by weight of 4-[naphtho(1,2)triazolyl(2)]aniline was dissolved in 100 parts of ethanol. About 1 part by weight of this solution was added to 50 parts of hot water containing 0.2-0.3% by weight of soap flakes sold under the trade name of Arctic Crystal Soap Flakes. A swatch of acetate rayon cloth was then stirred for a few minutes in this aqueous dispersion, removed, rinsed in hot water, and dried. The fabric showed a very bright fluorescence under ultraviolet light and was whiter in daylight than the untreated cloth.

Similar applications to nylon resulted in whitening of the fabric.

EXAMPLE IX

About 1 part by weight of a solution of 5 parts of 3-chloro-4-[naphtho(1,2)triazolyl(2)]aniline in 100 parts of isopropanol was added to 50 parts of hot water containing 0.2-0.3% by weight of a synthetic detergent sold under the brand name of Tide. A swatch of acetate rayon was treated as in Example I. The fabric was of improved whiteness and showed a strong blue fluorescence under ultraviolet light.

Similar application of the brightening agent to viscose rayon resulted in improved whiteness.

EXAMPLE X

About 1 part by weight of a solution of 0.5 part of 3-methyl-4-[naphtho(1,2)triazolyl(2)]aniline in 100 parts of ethanol was added to 50 parts of hot water containing 0.2-0.3% by weight of a synthetic detergent of the alkyl phenol-ethylene oxide type. A swatch of nylon taffeta, type 200, treated as in Example I showed a very bright fluorescence under ultraviolet light and was of improved whiteness.

Swatches of acetate rayon were treated in a similar manner. All fabrics showed improved whiteness.

EXAMPLE XI

A swatch of acetate rayon was treated with a brightening composition prepared as in Example VIII except that 3-methoxy-4-[naphtho(1,2)triazolyl(2)]aniline was used in place of 4-[naphtho(1,2)triazolyl(2)]aniline. The fabric was of improved whiteness. Nylon treated in this manner also showed improved whiteness.

EXAMPLE XII

To a stirred mixture of 50 parts of water and 50 parts of soap flakes sold under the trade name Arctic Crystal Soap Flakes was added a solution of 2.5 parts of N,N-dimethyl-4-[naphtho(1,2)triazolyl(2)]aniline in 25 parts of ethanol. After stirring the mixture well for several minutes, the water and ethanol were removed by distillation under slightly reduced pressure. About 1 part of the resulting soap flakes was added to 500 parts of hot water. A large swatch of acetate rayon was added, stirred for several minutes, removed, rinsed with hot water, and dried. The fabric showed a very bright blue fluorescence under ultraviolet light and was of improved whiteness. Nylon was also treated in this manner to yield a fabric of improved whiteness.

EXAMPLE XIII

To a stirred mixture of 50 parts of water and 50 parts of synthetic detergent sold under the trade name of Tide was added a solution of 2(N-morpholinylphenyl)-naph-

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tho(1,2)triazole in 25 parts of ethanol. The water and ethanol were removed under slightly reduced pressure. A swatch of nylon was treated with the resulting detergent containing the brightening agent by the procedure of Example XII to give improved whiteness. The whiteness of acetate rayon was also improved by similar treatment.

EXAMPLE XIV

Example VIII was repeated with the exception that 0.5 parts by weight of 4-[naphtho(1,2)triazolyl(2)]aniline was replaced by an equivalent weight of N,N-bis β -cyanoethyl-4-[naphtho(1,2)triazolyl(2)]aniline. The acetate rayon fabric showed improved whiteness. Nylon treated in this manner also showed an improved whiteness.

In order to further determine the efficiency of the brightening compositions of the present invention, the brighter photometer tests were conducted as follows:

The weight of the test swatches is approximately 5 grams $\pm$ 0.05 gram. The nylon swatches are cut to size approximately 8 $\frac{3}{4}$ " x 9" and the rayon to approximately 7 $\frac{3}{8}$ " x 7 $\frac{3}{4}$ ".

14 grams of unbrightened (containing no brightening agent) soap powder sold under the trade name of "Dreft" was dissolved in distilled water in a 1000 ml. volumetric flask and brought to volume at room temperature.

70 mg. of each of the brightening agents of Examples I to VII inclusive were weighed out separately on hot watch glasses. Each sample of the brightening agent was transferred to a 100 ml. volumetric flask (low actinic glass) with a small funnel and the sample washed down into the flask with ethyl alcohol. The flask was filled approximately half full with the alcohol. After the sample is not in solution, the flask may be heated on a hot plate and the volume in the flask brought to room temperature and filled up to melt with alcohol. It is to be noted that the preparation of brightener solution should be carried out in a dark room or under a curtained hood which emits no ultraviolet light. The solution prior to testing should be stored in the dark.

In order to use the solutions, the concentration of the brightening agent should be 0.7 gram per liter. For spectrophotometric solutions, it is necessary to prepare a solution at concentration of 0.025 gram per liter from the above solutions.

The test is carried out as follows:

2 ml. of the alcohol soluble sample solution, 54 ml. of additional alcohol are added to make a total volume of 56 ml. It is to be further noted that with some solvents, such as acetone, glacial acetic acid, methyl diformamide, etc. a spectrophotometric curve cannot be obtained over the entire ultraviolet range, due to the "cut-off point" of the solvent. These solutions should be prepared and kept in flasks of low actinic glass.

To apply the solutions to the test cloth, the following procedure is employed:

Add to clean one-pint Launder-Ometer jars 10 $\frac{1}{4}$ " stainless steel balls. Add in succession the requisite amount of detergent solution and distilled water (Table I); deliver the detergent solution by pipette and the water by automatic burette. Place the jars in the preheating bath of the Launder-Ometer and add (by pipette) the required amount of brightener solutions. Shake each jar on addition of brightener to mix solutions. When the jars are in temperature, add one 5-gram swatch to each jar, closing jar and shaking until swatch is immersed. Place jars in Launder-Ometer for 20 minutes at 100° F.

At the end of the running time discharge the samples into a strainer to separate the steel balls. Squeeze the soap solution from swatch by hand. Rinse each swatch in its jar twice in lukewarm water, swishing the swatch up and down 5 times in the water, refilling the jar for each rinse, and squeeze the swatch after each rinse. Clip to clothespins strung on a wire and air dry at room temperature, with black curtain to exclude U. V.

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Table I

Percent Brightener based on—		Brightener per jar (water solution)		Distilled Water ml.	Detergent Soln. 1.4%, ml.
Soap	Cloth	ml.	mg.		
0.05	0.0035	2.5	0.175	72.5	25
0.1	0.007	5.0	0.350	70.0	25
0.2	0.014	10.0	0.700	65.0	25
(Solvent Solution)					
0.05	0.0035	0.25	0.175	74.75	25
0.1	0.007	0.5	0.350	74.5	25
0.2	0.014	1.0	0.700	74.0	25

Weight of cloth..... 5 grams.
 Total volume of liquor..... 100 ml.
 Cloth to liquor ratio..... 1.20.
 Detergent:
 based on liquor..... 0.35%.
 based on cloth..... 7.0%.
 Temperature of application..... 100° F.
 Rinse..... 2 rinses in lukewarm tap water.
 Dry..... air dry at room temperature.

The measurement of the reflectance and the brightness of the treated samples on the fluorescence photometer was made for each of the brightening agents of Examples I 25 to VII inclusive while averaging four readings for a measurement. The swatches were also compared to standards under north light and ultraviolet light. The results obtained are shown in Table II.

Table II

Example	Fabric	Percent OWS	Brightness Reading	Remarks (Shade of Fluorescence)
1	nylon	0.1	50.1	Good shade of fluorescence on nylon and acetate. Not as violet as the standard.
	do	0.2	73.9	
	acetate—dull	0.1	35.5	
	acetate—glossy	0.1	41.6	
	acetate—dull	0.2	53.5	
2	nylon	0.2	64.3	Similar to Example 1.
	acetate—dull	0.2	31.5	
	acetate—glossy	0.2	17.4	
	acetate—dull	0.2	20.5	
	acetate—glossy	0.2	41.7	
3	nylon	0.2	18.2	Greener shade of fluorescence than Example 1.
	acetate—dull	0.2	23.3	
	acetate—glossy	0.2	24.0	
	acetate—dull	0.2	7.5	
	acetate—glossy	0.2	10.0	
4	nylon	0.1	42.2	Similar to Example 1.
	do	0.2	59.0	
	acetate—dull	0.1	40.0	
	acetate—glossy	0.1	47.9	
	acetate—dull	0.2	60.0	
5	nylon	0.1	72.5	Shade of fluorescence much greener than Example 1.
	do	0.2	28.1	
	acetate—dull	0.2	43.2	
	acetate—glossy	0.1	29.0	
	acetate—dull	0.2	35.6	
6	nylon	0.2	46.4	Shade of fluorescence only slightly greener than Example 1.
	acetate—glossy	0.2	57.2	
	nylon	0.1	13.0	
	do	0.2	21.6	
	acetate—dull	0.1	20.8	
7	acetate—glossy	0.1	25.9	Shade of fluorescence similar to Example 1.
	acetate—dull	0.2	31.1	
	acetate—glossy	0.2	39.6	
	nylon	0.1	20.3	
	do	0.2	33.2	
Standard (4-methyl-7-diethylamino-coumarin)	acetate—dull	0.1	29.8	Pronounced violet shade, particularly on acetate. Shade objectionable at high concentrations—Much less bright than Examples 1; 5.
	acetate—glossy	0.1	35.5	
	acetate—dull	0.2	47.9	
	acetate—glossy	0.2	56.6	
	acetate—dull	0.1	56.6	

Synthetic detergent: Sodium lauryl sulfate.
 OWS = Percent by weight of brightener based on weight of detergent.
¹ Reading taken on dull side of acetate swatch.
² Reading taken on glossy side of same acetate swatch as (¹).

From the foregoing examples it becomes clearly manifest that the brightening compositions of the present invention produce a very pleasing shade of fluorescence on nylon and rayon fabrics, which does not have the violet cast or tint produced by many of the prior art brighteners, as shown in Table II. This violet cast is more noticeable on rayon acetate than on nylon. The shades of fluorescence of the compositions of the present invention are

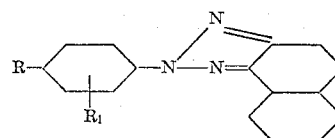
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greener than many of the commercial acetates and nylon brighteners, and may be used successfully in mixtures with brighteners, and may be used successfully in mixtures with brighteners possessing violet or pink shades of fluorescence resulting in an improved blue. Conversely the brightening compositions of the present invention are useful (for tinting) in conjunction with "pink" brighteners, and the pinkness is less objectionable.

The proportions of the brightening compositions of the present invention whether an individual compound or mixture thereof, may range from 0.005–0.01% by weight in an aqueous emulsion containing 0.1–2.5% by weight of an organic water-soluble synthetic detergent.

We claim:

1. A composition of matter for brightening white synthetic fibrous materials selected from the class consisting of synthetic fibrous superpolyamides and synthetic fibrous materials of organic derivatives of cellulose comprising an aqueous emulsion containing 0.1–2.5% by weight of an organic water-soluble synthetic detergent, and from 0.0005–0.01% by weight of a brightening agent characterized by the following general formula:



where R represents a member selected from the class consisting of amino, N,N-dialkylamino, N,N-bis-β-cyanoethylamino and N-morpholino radicals, and R₁ represents a member selected from the class consisting of hydrogen, lower alkyl, lower alkoxy, and halogen.

2. A composition of matter according to claim 1 wherein the brightening agent is 4-[naphtho(1,2)triazolyl(2)]aniline.

3. A composition of matter according to claim 1 wherein the brightening agent is 3-chloro-4-[naphtho(1,2)-triazolyl(2)]aniline.

4. A composition of matter according to claim 1 wherein the brightening agent is 3-methyl-4-[naphtho(1,2)-triazolyl(2)]aniline. 5

5. A composition of matter according to claim 1 wherein the brightening agent is 3-methoxy-4-[naphtho(1,2)-triazolyl(2)]aniline.

6. A composition of matter according to claim 1 wherein the brightening agent is N,N-dimethyl-4-[naphtho(1,2)-triazolyl(2)]aniline.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,842,501

July 8, 1958

Harlan B. Freyermuth et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 6, for "limited" read -- limiting --; column 8, line 11, for "0.005" read -- 0.0005 --.

Signed and sealed this 2nd day of December 1958.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents