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2,734,871

WHITE FLUORESCING MARKING INKS FOR TEXTILE IDENTIFICATION

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3 Claims. (Cl. 252—301.2)

This invention relates to white fluorescent dyestuffs and textile marking inks made therefrom which are normally colorless when viewed under normal light but fluoresce white when viewed under ultra violet light, and it particularly pertains to laundry marking inks composed of one or more of said white fluorescent dyestuffs dissolved in a carrying vehicle suitable for application of said ink to the textile material by any suitable mechanical marking means.

Fluorescent dyestuffs have been applied to textile materials to impart colored fluorescence thereto when illuminated by ultra violet light. Such fluorescent dyed textile materials are intended to be decorative or clearly visible in ultra violet light, and a sufficient amount of dyestuff is applied to impart a brilliant fluorescence when said dyed textiles are subjected to ultra violet light. The normal color or appearance of such fluorescent dyed textile materials under ordinary light is not important. Then, too, optical bleaches have been applied to white textile materials to whiten them and eliminate an off-white or yellowish tint. Dyestuffs for this purpose have sometimes been referred to as "white" dyes or dyestuffs, but this is somewhat of a misnomer since such reference is to the effect produced on the white textile materials rather than to the fluorescent color of the dyes or dyestuffs. The fluorescent color of the dyestuffs used for this purpose is not white but colored, their usual fluorescent color being blue, and, therefore, properly referred to as a blue fluorescent compound (Patent No. 2,528,323) or a colored or non-white fluorescent compound.

Fabric articles to be laundered, or some of the yarns or fibers thereof, may have been optically bleached and with different fluorescent colors. Obviously, it would be a most cumbersome and burdensome task if each article to be laundered had to be first subjected to an ultra violet light to determine whether or not it had been optically bleached to identify its fluorescent color, if optically bleached, and then be marked with a normally colorless marking ink having a fluorescent color contrasting with the fluorescent color of the article. Moreover, in addition to this inspection for determining the fluorescent color or colors of the articles to be laundered, many marking inks of different fluorescent colors would need to be used for marking the different fluorescent colored fabrics with the suitable contrasting one. Obviously a fluorescent ink of a character that would be suitable for marking all fabric articles, whether they are optically bleached or not, would be most desirable, yet the production of such a normally colorless dyestuff has not been heretofore attained.

Optical dyestuff bleaches are normally colorless and invisible when applied to a textile. While normally colorless and invisible on the textiles, they fluoresce with a blue to violet coloration when exposed to ultra violet rays. White textile fabrics when so bleached normally appear whiter. Blue fluorescent bleaches counteract the natural yellowishness or off-white color tint and increase the brilliancy of the fabric. Such bleaches are commonly used by commercial laundries and by original textile

2

manufacturers to improve the white appearance of the white textile fabrics and the pastel colors under natural light. The bleaches are separate preparations or may be included in the soap or cleaning agents. Accordingly, the vast majority of white and pastel colored fabrics are highly fluorescent when viewed under ultra violet light, but, without exception, all such bleaches fluoresce in various shades of blue to violet, and they are intended to do so.

Whether or not the fabrics are originally optically bleached, they may be subsequently bleached in a laundering operation, and, if the previous original bleaching dyestuffs or subsequently applied ones are not removed, there may well be several fluorescent colors in any one or more of the fabrics. It is also a fact that all of the fluorescent dyestuffs heretofore used in normally colorless marking inks also fluoresce in shades of blue to violet. Therefore, if any optically bleached textile fabric is marked with a normally colorless blue fluorescent dyestuff, it is not visible under an ultra violet light because its fluorescent spectrum is enveloped or blended in the fluorescent spectrum of the optical bleach of the textile. It is obliterated by the fluorescent spectrum of the optical bleach. The problem is comparable to, and has its counterpart, by way of example, in the visible spectrum. A visible marking ink of the same color as the fabric to be marked would not be visible and would likewise be obliterated because there is no color contrast between the fabric and the mark.

This problem has now been overcome by the present invention of a white fluorescent dyestuff for use in laundry marking inks. Accordingly, plain or non-optically bleached fabrics, as well as optically bleached ones, can be marked in accordance with my invention, and the marking, viewed under ultra violet light, will fluoresce in contrast with the fluorescent color or colors of the optically bleached textile fabric as well as in contrast with the natural colors of non-optically bleached textile. And it matters not that the fabrics to be marked have been repeatedly optically bleached.

There is, so far as I am aware, no white fluorescent dyestuff or marking ink, or one which fluoresces white when subjected to ultra violet light. Consequently none of this character has been available for the manufacturer of textile marking inks, such as are used for marking fabric articles to be laundered.

Accordingly, one of the objects of the invention is the production of normally colorless dyestuff which fluoresces white under ultra violet light.

Another object of the invention is the production of an ink which is suitable for marking all textiles, white or colored, and irrespective of whether or not any or all of said textiles are optically bleached.

Another object of the invention is the production of a normally colorless dyestuff, and marking ink composed thereof, which is indelible enough to withstand at least one laundering.

Another object of the invention is the production of a dyestuff derivative, and textile marking ink composed thereof, comprised of an aromatic molecular structure having groups disposed to impart a white fluorescence to the dyestuff.

Another object of the invention is the production of a dyestuff derivative, and textile marking ink composed thereof, comprised of an aromatic molecular structure having opposite terminal groups which impart a white fluorescence to the dyestuff.

Another object of the invention is the production of an amino stilbene dyestuff derivative, and textile marking ink composed thereof, having an aromatic polyacyl molecular structure of sufficient length to impart a white fluorescence to the dyestuff.

Still another object of the invention is the produc-

3

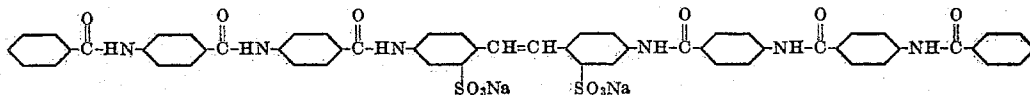
tion of an amino stilbene dyestuff derivative, and textile marking ink composed thereof, having aromatic and non-aliphatic acyl groups as the opposite terminals of the linear molecular structure.

Still another object of the invention is a stilbene dye-stuff derivative having the characteristic of fluorescing white under ultra violet light and being an amino stilbene compound structurally extended in such a way as to impart the characteristic of white fluorescence.

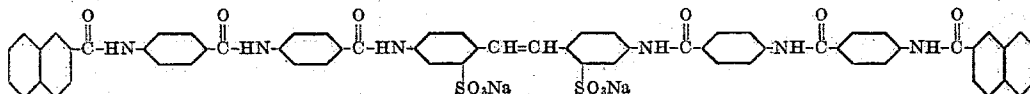
Further objects, and objects relating to details of composition and economies of operation, will readily appear from the detailed description to follow.

In one instance, I have accomplished the objects of my invention by the dyestuff and marking ink compositions set forth in the following specification. My invention is clearly defined and pointed out in the appended claims. Dyestuffs constituting preferred embodiments of my invention, as well as marking inks formed thereof, are set forth in the specification, but it will be understood that these typify the invention generically, and that the invention is not limited to the specific embodiment disclosed for typifying the invention.

The invention, broadly described, comprises an amino stilbene dyestuff derivative having a linear aromatic polyacyl extended molecule that causes the said dyestuff de-



riative to fluoresce white. The terminal groups are typified generally by acyl groups which are aromatic and not aliphatic, with or without the auxochrome groups included therein. Acyl groups, without the inclusion of

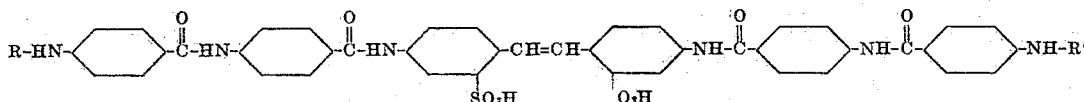


the auxochrome groups, are preferred as the terminals of the molecule, but the invention, in its broadest aspect, is directed to any opposite terminal groups in the linear aromatic molecular extension which impart a white fluorescence. Accordingly, the acyl groups as the opposite end terminals of the stilbene dyestuff derivative are representative of and typify any end terminal linear groups which impart the characteristic of a white fluorescence and are normally colorless in the visible spectrum. The dyestuff is also indelible when applied to textiles as a marking ink.

Auxochrome groups, such as hydroxyl, amino, sulfo, carboxy or the like, may be present on the terminal aromatic rings, but, since they tend to decrease the intensity of fluorescence, they preferably are omitted altogether from said acyl groups.

A suitable ink for marking textile fabrics is formed by dissolving the novel white fluorescent dyestuff stilbene derivative in a suitable carrying vehicle commonly used for making colorless fluorescent inks as in U. S. Patent No. 2,267,758, which is referred to and incorporated here as a part of the present invention for a disclosure of suitable liquid vehicles for colorless fluorescent marking dyestuffs in laundry marking inks.

More specifically described, the novel dyestuff is a derivative of the base stilbene compound 4:4'-di-p-aminobenzoylaminobenzoylamino - stilbene - 2:2' - disulfonic acid, having the following structural formula:

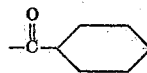


This base stilbene compound, and method of forming it, is disclosed by Otto Lang on page 233 of *Die Zwischenprodukte der Teerfarbenfabrikation*, published by Otto Spamer, Leipzig, Germany. This base compound

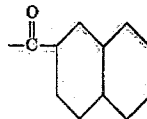
4

fluoresces blue. Acyl chloride is reacted in an aqueous media with aryl amine, the base stilbene compound, in the presence of alkali to produce opposite terminal groups thereon of benzoyl or b-naphthoyl.

5 The R, R' of the opposite terminal groups benzoyl has the following structural formula:

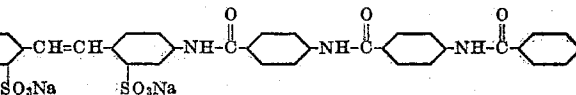


¹⁰ The R, R' of the opposite terminal groups b-naphthoyl has the following structural formula



Typifying and representative of the invention are the following dyestuff examples as specific embodiments, 20 these being the base stilbene compound with the terminal acyl groups as set forth above.

Example No. 1 is the compound 4:4'-Di-p-(benzoylaminobenzoylaminobenzoylamino) - stilbene - 2:2' - disodium sulfonate having the structural formula:



Example No. 2 is the compound 4:4'-Di-p-(b-naphthoylamino)benzoylamino) - stilbene - 2:2'-disodium sulfonate having the following structural formula:

The specific method for forming above Example 1 is 40 as follows with the parts and percentages given by weight and the temperature scale in centigrade.

Five parts 4:4'-di-p-aminobenzoylamino benzoylamino-
stilbene-2:2'-disodium sulfonate as a 5% glycerol solu-
tion is mixed with 2 parts benzoic anhydride as a 10%
glycol ether (e.g. ethylene glycol monobutyl ether) solu-
tion. With vigorous stirring the mixture is heated to be-
tween 90 to 100°. The mixture is held at this temper-
ature range for ½ hour or until clarification is observed.
The resultant concentrated dye solution upon cooling may
be used directly in preparing the ink.

This procedure eliminates the bothersome and time-consuming separation and drying operations. If, however, the solid product of the reaction is desired, 1 part concentrated dye solution is diluted with 2 parts ice water, and the resultant precipitate is filtered free and dried.

The specific method for forming above Example 2 is as follows with the parts and percentages likewise given by weight and the temperature scale in centigrade.

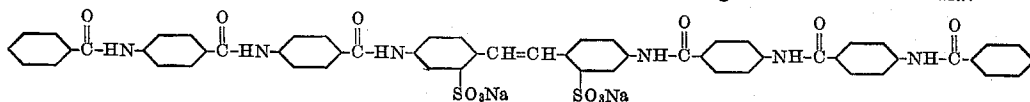
Five parts 4:4'-di-p-aminobenzoylamino benzoylamino-
stilbene-2:2'-disodium sulfonate as a 5% glycerol solu-
tion is mixed with 3 parts b-naphthoyl chloride as a 10%
glycol ether (e. g. ethylene glycol monobutyl ether) solu-
tion. At 20° the mixture is vigorously stirred for 1/2
hour. 1 part triethanolamine (or suitable organic base)
is added and the mixture is heated for solution. The re-

sultant concentrated dye solution upon cooling may be used directly in preparing the ink. If the solid product is desired, it is separated as in Example No. 1.

75 In preparing an ink the desired amount of dyestuff em-

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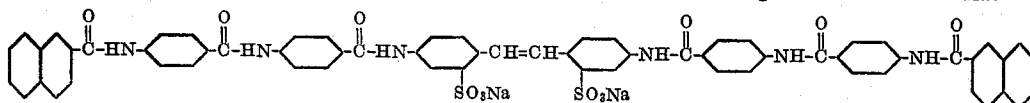
bodying the invention is dissolved in a suitable solvent. The solvent is merely a liquid vehicle carrier for the dyestuff and may be of the character as that now commonly used for fluorescent marking inks for fabrics. Ordinarily,



the vehicle has a concentration of about five-tenths (0.5%) percent dyestuff of the character described.

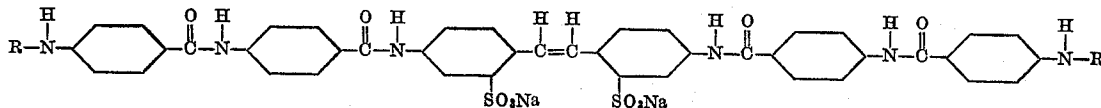
One preferred formula for compounding the ink is as follows:

White fluorescent dyestuff	percent	0.5
Glycerine	parts	40
Isopropyl alcohol	do	15
Ethylene glycol monobutyl ether	do	45



From the foregoing description and the specific examples of dyestuffs and ink formed therefrom, it will be seen that I have produced a dyestuff derivative which fluoresces white, this being typified by the two examples. The opposite terminal acyl groups represent and typify any terminal groups which will lineally extend the dyestuff molecule and cause the dyestuff to fluoresce white.

I am aware that there may be various changes in de-



tails of construction and composition of both the dyestuff and the ink without departing from the spirit of my invention, and, therefore, I claim my invention broadly as indicated by the appended claims.

Having thus described my invention, what I claim as new and useful and desire to secure by United States Letters Patent, is:

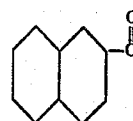
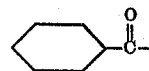
1. An ink for textile identification consisting essentially of a liquid carrying vehicle of a viscosity and drying rate suitable for use in a marking device, and a normally invisible dyestuff compound dissolved in the liquid ve-

hicle, said dyestuff compound having a white fluorescence under ultra-violet light and comprising 4:4'-Di-p-(benzoylamino benzoylamino benzoylamino) - stilbene - 2:2'-disodium sulfonate having the structural formula:

2. An ink for textile identification consisting essentially of a liquid carrying vehicle, of a viscosity and drying rate suitable for use in a marking device, and a normally invisible dyestuff compound dissolved in the liquid vehicle, said dyestuff compound having a white fluorescence under ultra-violet light and comprising 4:4'-Di-p-(benzoylamino benzoylamino benzoylamino) - stilbene - 2:2'-disodium sulfonate having the structural formula:

3. An ink for textile identification having a liquid carrying vehicle, of a viscosity and drying rate suitable for use in a marking device, and a normally invisible dyestuff compound dissolved in the liquid vehicle, said invisible dyestuff compound characterized by white fluorescence under ultraviolet light and consisting of an aromatic polyacyl derivative of diamino stilbene disulfonic acid having the general structural formula

where R is a member of the class consisting of



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