

1

3,826,609

METHOD OF DYEING SYNTHETIC FIBERS AND BLENDS

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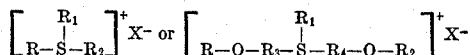
Int. Cl. D06p 3/82, 1/76

U.S. Cl. 8—21 R

5 Claims

ABSTRACT OF THE DISCLOSURE

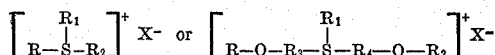
A method of dyeing a textile fiber selected from the group consisting of a modified polyester, polyvinyl chloride, polyacrylonitrile and cellulose acetate fibers, which comprises dyeing the fibers with an anionic dyestuff in the presence of at least one compound selected from sulfonium salts of the formula



wherein R, R₁ and R₂ are each selected from the group consisting of alkyl, alkenyl, cycloalkyl, aryl and aralkyl groups of 1-18 carbon atoms, R₃ and R₄ are each alkyl groups of 1-5 carbon atoms and X is selected from the group consisting of halogens, alkoxy sulfate and OH group.

This application is a division of application Ser. No. 804,294 filed Mar. 4, 1969, now U.S. Pat. 3,666,403.

This invention relates to a method of dyeing modified polyester, polyvinyl chloride, polyacrylonitrile or cellulose acetate fibers with the anionic dyestuffs. More particularly, this invention relates to a method of dyeing a fiber selected from the group consisting of the modified polyester, polyvinyl chloride, polyacrylonitrile and cellulose acetate fibers with an anionic dyestuff in the presence of at least one compound selected from sulfonium salts of the formula



wherein R, R₁ and R₂ are each selected from the group consisting of alkyl, alkenyl, cycloalkyl, aryl and aralkyl groups of 1-18 carbon atoms, R₃ and R₄ are each alkyl groups of 1-5 carbon atoms and X is selected from the group consisting of halogens, alkoxy sulfate and OH group.

Fibers manufactured from such synthetic polyesters as polyethylene terephthalate do not have any affinity at all for the ionic dyestuffs and, accordingly, they were previously dyed principally by means of disperse dyes. However, disperse dyes are costly and moreover the dyed products obtained by their use were not satisfactory with respect to brightness. Therefore, there was a strong demand in the trade for the modification of the polyester fibers so that they could be dyed by means of ionic dyestuffs, particularly acid dyes. It is therefore a primary object of this invention to provide a method by which modified polyester can be dyed to deep shades.

Numerous methods of dyeing polyvinyl chloride fibers are known. For instance, there is a dyeing method which comprises preparing an insoluble complex with an acid dye and a cationic surfactant and using this complex for dyeing the fiber; however, none of the conventional methods have been able to provide dyed products which are

2

fully deep in shade. Therefore, a second object of the invention is to provide a dyeing method by which polyvinyl chloride fibers can be dyed to fully satisfactory deep shades.

5 Polyacrylonitrile fibers are usually dyed with cationic dyestuffs. However, in this case also, when expansion of the scope of color and when the case of dyeing of mixed spun products are considered, the impartation of dyeability by means of the acid dyes is desirable. A third object of the present invention is therefore to provide a dyeing method which expands the scope of color of the dyed products of polyacrylonitrile fibers as well as facilitates the dyeing of mixed spun products, especially mixed spun products with wool.

15 Cellulose acetate fibers are also dyed with disperse dyes as in the case with polyester fibers, but in this case also the shortcoming was noted that the brightness of the dyed product was not yet fully satisfactory. A fourth object is therefore to provide a dyeing method which can impart excellent dyeability to cellulose acetate fibers and dye these fibers to bright shades.

Other object and advantages of this invention will become apparent from the following description.

Research was conducted both from the aspect of the 25 modification of the polyester fiber and the method of dyeing the same. As a consequence, it was found that shaped articles of certain classes of modified polyesters could be dyed to exceedingly deep shades when dyed by the anionic dyestuffs in the presence of at least one compound selected from the above defined sulfonium salts.

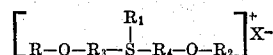
The sulfonium salts to be used in the present invention are compounds having the hereinbefore indicated formulae. As specific compounds, in the case, for example, 35 where R, R₁ and R₂ of the foregoing formulae are saturated hydrocarbon residues, included are such as the dimethylstearylsulfonium salt, methylethyl-laurylsulfonium salt, methylpropyl-laurylsulfonium salt, methylbutyl-laurylsulfonium salt, ethylpropylstearylsulfonium salt, tributylsulfonium salt, dibutylpropylsulfonium salt and diethylcyclohexylsulfonium salt.

On the other hand, as examples of unsaturated hydrocarbon residues, there are the alkenyl or the aryl or aralkyl groups such as phenyl, benzyl, naphthyl and naphthylmethyl. For example, mention can be made of 45 such as the

dimethylbenzylsulfonium salt,
diethylbenzylsulfonium salt,
dibutylbenzylsulfonium salt,
50 methylethyl-naphthylsulfonium salt,
ethylaryl-laurylsulfonium salt,
methylbutyl-oleylsulfonium salt,
ethylpropylphenylsulfonium salt and
diarylmethylsulfonium salt.

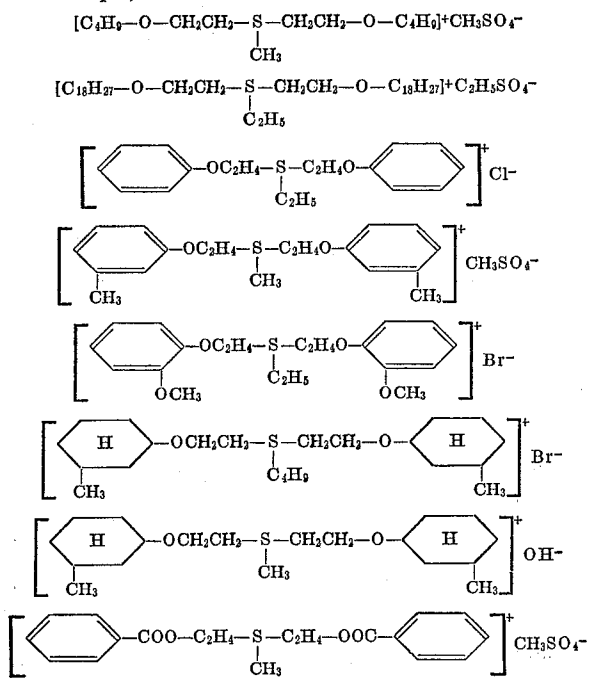
55 Further as derivatives of saturated or unsaturated hydrocarbon residues, those hydrocarbon residues having substituents on their side or straight chain are useable. The substituents include such as alkyl, aryl, alkenyl, nitro, alkoxy, halogens, cyano-carboxy and sulfonic acid. Needless to say, the substituents are not restricted to those mentioned above. As these derivatives, included are such, for example, as dimethyl 4-chlorobenzylsulfonium salt, 60 methylethyl 2-methoxybenzylsulfonium salt, diethyl 4-methylnaphthylmethylsulfonium salt and dibutyl 4-carboxylbenzylsulfonium salt.

On the other hand, the one other class of sulfonium salts to be used in this invention is that having the hereinbefore indicated formula



70

As specific compounds, included in this case are such, for example, as follows:



Polyesters, as used herein, are principally intended to be polyethylene terephthalate. However, the expression "polyester" also refers to those polyesters which comprise at least 60 mol percent of ethylene terephthalate units and in which a part of the acid or dihydroxy component is substituted by one or more classes of either difunctional or hydroxy acids such as isophthalic acid, compounds having metal salts of sulfonic acid, beta-hydroxyethoxybenzoic acid, p-hydroxybenzoic acid, diphenyldicarboxylic acid, naphthalenedicarboxylic acid, diphenylsulfonedicarboxylic acid, adipic acid and sebacic acid, or the aliphatic, alicyclic and aromatic dihydroxy compounds such as diethylene glycol, trimethylene glycol, hexamethylene glycol, neopentylene glycol, 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethylcyclobutanediol-1,3, 1,4-bis(hydroxyethoxy)benzene, bisphenol A and compounds having the tertiary amino group [i.e. butyldi(beta-hydroxyethyl)amine]. Further, polyesters in which a minor proportion of a monofunctional compound such as benzoylbenzoic acid and/or a polyfunctional compound of above trifunctional such as pentaerythritol and trimesic acid are copolymerized to a certain extent with substantial cross-linking are applicable. In the preparation of these polyesters, the known catalysts and additives such as stabilizers, delustrants, etc., can be added with no trouble at all.

The term "modified polyester composition," as used herein, refers to the blended composition of a polyamide and a polyester obtained as hereinbefore described, the blended composition of a polyamide and a copolyester obtained by copolymerizing a polyalkylene glycol with a polyester, the blended composition of a polyester and a polyamide blend containing a polyalkylene glycol, and the blended composition of a polyester, polyamide and polyalkylene glycol. Modified polyester fibers which are particularly desirable include: (a) those obtained by melt-spinning a blended composition of 60–99.5 wt. percent of a polyester and 40–0.5 wt. percent of a polyamide and drawing the resulting filaments; (b) those obtained by melt-spinning a blended composition of 40–0.5 wt. percent of a polyamide with 60–99.5 wt. percent of a copolyester obtained by copolymerizing with a polyester 1–35 wt. percent, based on the overall weight of the composition, of a polyalkylene glycol and drawing the resulting filaments; (c) those obtained by melt-spinning a blended composition of 99.5–60 wt. percent of a poly-

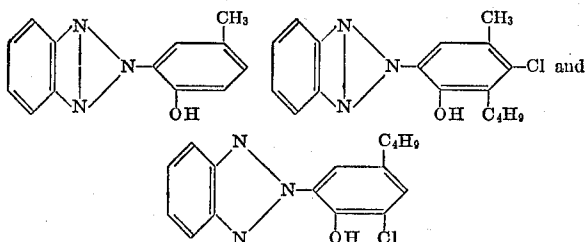
ester and 0.5–40 wt. percent of a polyamide blend containing, based on the overall weight of the composition, of 1–30 wt. percent of a polyalkylene glycol, and drawing the resulting filaments; (d) those obtained by melt-spinning a blended composition consisting of 60–99.5 wt. percent of a polyester, 0.5–40 wt. percent of a polyamide and 0.6–30 wt. percent of a polyalkylene glycol and drawing the resulting filaments; (e) those obtained by melt-spinning a blended composition of 60–99.5 wt. percent of a polyester and 40–0.5 wt. percent of a polyamide and drawing the resulting filaments, then shrinking the filaments by heat treating them and thereafter redrawing the filaments; (f) those obtained by melt-spinning a blended composition of 60–99.5 wt. percent of a polyester and 40–0.5 wt. percent of a polyamide, and drawing the resulting filaments, then shrinking the filaments 2 to 50% at a temperature ranging between 140° C. and the melting temperature of the polyester fiber and thereafter redrawing the filaments; and (g) those obtained by melt-spinning a blended composition of 60–99.5 wt. percent of a polyester and 40–0.5 wt. percent of a polyamide and drawing the resulting filaments, followed by shrinking the filaments by heat treating them and thereafter redrawing the filaments at a temperature ranging between room temperature and 230° C. and a draw ratio ranging from 2% to the point at which breakage of the polyester fiber takes place.

The manufacture of a fiber by melt-spinning and drawing a blended composition of a polyester and some amount of polyamide is known (British Patent Specification No. 610,140). However, the fiber which has been merely melt-spun and drawn in this manner does not demonstrate desirable dyeability when the usual method of dyeing it with anionic dyestuffs is employed. It is only when the fiber is dyed by the dyeing method of the present invention that it is possible to provide products dyed to bright and deep shades so as to be very useful.

As a result of further research with a view to improving the dyeability of the fiber itself obtained from the polyester polyamide composition, it was found that when one of the methods of the present invention, i.e., that wherein the fiber formed by melt-spinning and drawing the aforementioned polyester composition is then shrunk 2–50% at a temperature ranging between 140° C. and the melting temperature of the polyester fiber, and thereafter it is again drawn at a temperature between room temperature and 230° C. and a draw ratio ranging between 2% and the point at which its breakage takes place is employed and the so obtained fiber is used in combination with an anionic dye and at least one compound selected from the aforementioned sulfonium salts, dye products which are of greater brightness and of deeper shades can be obtained. Accordingly, the hereinabove indicated heat treatment and redrawing conditions are both critical. Thus, fibers having excellent dyeability cannot be obtained in those cases where either one of these conditions are lacking.

Further, ultraviolet absorbents can be used in the dyeing method of the present invention for improving the light fastness of the dyed products. The following compounds can be used as ultraviolet absorbents in the present invention.

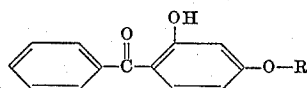
(1) 2-(2'-hydroxyphenyl)benzotriazole series, for example, those such as follows:



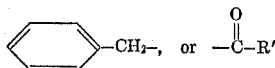
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(2) 2-hydroxybenzophenone series, for example, those of the following formulas:

(a)

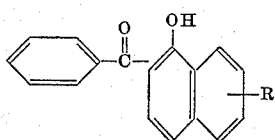


wherein R is H, $-C_nH_{2n+1}$ (wherein n is 1-18),



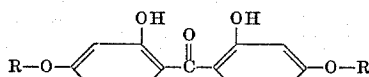
(where R' is alkyl or aryl); and

(b)

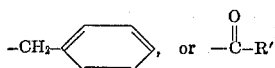


wherein R is H or $-SO_3H$.

(3) 2,2'-dihydroxybenzophenone series, for example, those of the formula

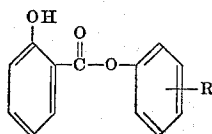


wherein R is H, C_nH_{2n+1} (wherein n 1-18),

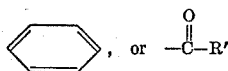


(where R is alkyl or aryl).

(4) Phenylsalicylic acid series, for example, those of the formula:

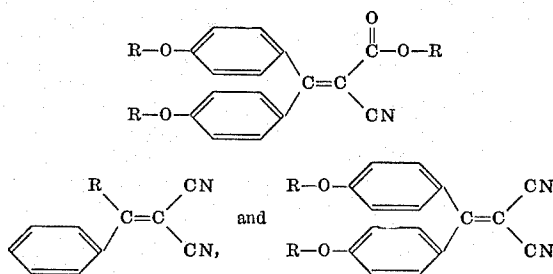


where R is H, C_nH_{2n+1} (where $n=1-18$),



(wherein R' is alkyl or aryl).

(5) Substituted acrylonitrile series, for example, those of the formulas:



wherein R is alkyl or aryl.

While the amount of these ultraviolet absorbents used will vary depending upon the class of the material to be dyed, the class of the dyestuff and the concentration and bath ratio etc., the use of about 1-10% (O.W.F.) based on the material to be dyed will do. It is also possible to achieve the result desired by imparting the ultraviolet absorbent to the fiber using a separate bath.

Again, the modified polyester composition of the present invention not only possesses excellent affinity for anionic dyestuffs, as noted hereinbefore, but also demonstrates satisfactory affinity for disperse dyes. In addition, it can also be dyed satisfactorily by means of the basic dyes in the presence of anionic substances. As anionic substances, included are inorganic acids such as sulfuric

6

and acetic acids and the salts thereof; and benzenesulfonic acid, toluenesulfonic acid, higher alkylbenzenesulfonic acid, and sulfuric esters of higher alcohols and the salts thereof; and phenols.

There are no particular restrictions as to the polyamides to be used in the present invention as long as they are serviceable with respect to their thermal resistance, etc. Mention can be made of such, for example, as polycaprolactam, polynaphthamide, polyundecamide, polyhexamethylene adipamide and polymetaxylene adipamide, or copolymers of these with other amide-forming substances. These polyamides can be used either alone or in combinations of two or more thereof. Of course, polyamides, the aromatic polyamides such, for example, as those which have copolymerized therewith the hexamethylene-diammonium terephthalate component give especially desirable results with respect to compatibility. These polyamides are incorporated in the polyester in an amount of 0.5-40% by weight, and preferably 5 to 35% by weight. If the content of polyamide is less than 0.5% by weight, the affinity of the resulting fiber for ionic dyestuffs is inadequate. On the other hand, if the content of the polyamide exceeds 40% by weight, the properties as a polyester fiber are lost. Accordingly, it is undesirable for the content of the polyamide to be outside the range indicated above.

In addition, the dyeability of the fiber can be further enhanced by incorporating in the foregoing polyesters and/or polyamides in an amount not exceeding 30% by weight, based on the overall weight of the fiber, a polyoxyalkylene glycol. As the polyoxyalkylene glycol, mention can be made of such, for example, as polyoxyethylene glycol, polyoxypropylene glycol, polyoxyethyleneoxypropylene glycol block or random copolymer, methoxypolyoxyethylene glycol, phenoxypolyoxyethylene glycol and octylphenoxypolyoxyethylene glycol. These polyoxyalkylene glycols may be present in either the polyester or the polyamide, or in both components. It may be added either during the early stages of the manufacture of the polyester or during the blending of the components.

It does not matter whether the polyvinyl chloride fiber used in the present invention is a homopolymer, a copolymer or an afterchlorinated product.

Good results can naturally be expected even if this method is applied to the mixed woven products of polyvinyl chloride fiber and other classes of fibers. Moreover, in the case of a mixed spun product of polyvinyl chloride fiber with wool, there is a great advantage in that the two fibers can be dyed with the same acid dye in a single bath.

As the polyacrylonitrile fibers to be used in the present invention, acrylic fibers that do not possess dye receptive sites are useable. Included are the Orlon (trademark of Du Pont Company) type, Dynel (trademark of Union Carbide and Chemical Company) type, and the acrylic conjugated fiber. Again, it goes without saying that the present invention also has applicability to the mixed textile products of the foregoing fibers with other classes of fibers.

As the cellulose acetate fibers to be used in the present invention, included are the usual diacetate to triacetate fibers. Again, the present invention can also be applied to the cellulose acetate fibers obtained by the after acetylation technique. Again, the invention can, of course, be applied to the mixed textile products of the foregoing fibers with other classes of fibers. The method of the present invention is especially effective in the case of a mixed product of acetate fibers with polyamide fibers, since both fibers are dyeable with acid dyes.

The modified polyester fibers that can be dyed by means of the method of the present invention are the so-called readily dyeable polyester fibers whose dyeability by means of disperse dyes has been improved, as hereinbefore described, by either an elevated temperature treatment or the introduction (blending or copolymerizing) of a third component. The term "readily dyeable polyester fibers," as used herein denote those fibers having a dye adsorption

of at least 60% as determined by the method of measurement of the rate of dye adsorption as defined below.

The rate of dye adsorption is determined in the following manner. The specimen is washed in 100-fold amount of distilled water (70° C.) for 30 minutes with stirring, followed by air drying and thorough opening of the fiber. One gram of the so standardized specimen is weighed and dyed under the following conditions:

After completion of the dyeing and cooling to room temperature, a suitable amount of the remaining dye liquor is taken and combined with an equal amount of C.P. acetone (reagent), following which this acetone-water (1:1) mixture is diluted 25 times and the optical density is measured using a spectrophotometer. Next, the before-dyeing dye liquor diluted in a similar manner is measured for its optical density. The rate of dye adsorption is then obtained by the following equation, the average of three measurements rounded to whole numbers being used.

$$\text{Dye adsorption (percent)} = \left(1 - \frac{d}{d_0}\right) \times 100$$

wherein d_0 = the optical density of the before-dyeing dye liquor and
 d = the optical density of the after-dyeing remaining liquor.

Polyester fibers having a dye adsorption of below 60% cannot provide satisfactory dyed products even though the method of the present invention is used.

If the present invention is applied to polyamide fibers (e.g. nylon) the results are negative. This is believed to be due to the fact that the dye is not dissociated as a result of the anionic dye forming a complex, with the consequence that in the case of the polyamide fibers having dye receptive sites the results are negative as a result in the decline in the dye adsorption.

Further, the anionic dyestuffs, as referred to herein, denote all of those dyes having an anionic group, i.e., the acid dyes, direct dyes, metal complex dyes, reactive dyes and acid mordant dyes.

In practicing the present invention, the dyeing methods that can be used include the various conventional methods such as the dip, padding and printing techniques.

The dyeing conditions will vary depending upon the class and form of the textile to be dyed and the class of dyeing method to be employed. For instance, in the case of the most widely practiced dip method, the dyeing conditions will be as indicated below.

In the case of the method of dyeing the modified polyester fiber, the aforementioned compounds are added to the dye bath in a concentration of 1-100% O.W.F. A dyeing temperature of below 100° C. does not result in a satisfactory dye adsorption, therefore, a temperature exceeding 100° C. is required. Usually, the dyeing is carried out at a temperature of 110-130° C. until the intended color deepness is obtained. Again, carrier dyeing can also be carried out effectively using carriers known conjointly. In addition, it is also possible to make conjoint use of the organic and inorganic acids or salts in carrying out the dyeing operation.

On the other hand, in the case of the method of dip dyeing polyvinyl chloride fibers, the dyeing may be carried out at 50-100° C. using the aforesaid compounds in a concentration of about 1-50% O.W.F. (percentage based on the weight of the material to be dyed), though varying depending upon the dyestuff used. Again, carrier dyeing can also be carried out effectively using known carriers conjointly.

Further, in the case of the cellulose acetate and polyacrylonitrile fibers, the amount of the compounds used will differ depending upon the concentration of the dyestuff used, but usually the amount ranges from 1% to 100%. A dyeing temperature in the range of 80-120° C. is convenient and, if possible, the higher, the better.

Again, carrier dyeing is also effectively carried out by conjointly using known carriers.

As such known carriers, mention can be made of the phenolic compounds such as o- and p-phenylphenol, the chlorobenzene type compounds such as monochlorobenzene, o-dichlorobenzene and trichlorobenzene, benzoic acid and benzoic acid type compounds such as benzoic acid, and the naphthalenic compounds such as methyl naphthalene. These carriers are added, for example, to the dye bath as an aqueous solution in the case of those which are water-soluble and as either a dispersion or emulsion in the case of those which are water-insoluble.

For carrying out level dyeing by dispersing the dyestuff thoroughly and for preventing the formation of tar, it is preferred to use a suitable nonionic surfactant in the method of the present invention. Surfactants such as indicated are those which are usually widely used as dispersants. Included are, for example, the polyethylene glycol type surfactants such as polyethylene glycol alkylamines, polyethylene glycol alkyl ethers and polyethylene glycol aliphatic acid esters, and the ether or ester type surfactants which contain the polyhydric alcohols such as sorbitan aliphatic acid esters and aliphatic acid monoglycerides as the hydrophilic group.

The textile which has been dyed in accordance with the method of the present invention is thoroughly soaped after its dyeing and thereafter submitted to reduction clearing, if necessary. The textile dyed by such method still retains adequate fastness even after it has undergone these after treatments.

While the particulars of the principle underlying the present invention are not clear, it is believed that the water dissolved or dispersed dyestuff forms a complex with the sulfonium compounds with the result that compatibility and affinity with respect of the hydrophobic fibers are created, the complex simultaneously functioning at times as a carrier at elevated temperature to become diffused into the interior of the fiber and result in the adsorption of the dye. Accordingly, the balance of the affinity between the dyestuff and the sulfonium compounds become an important factor that determines the dye adsorption. The effects contemplated by the present invention cannot be achieved by just the insolubilization of the dye but can only be attained, as hereinbefore indicated, in those cases where the specific compounds defined by the foregoing formula are used.

Also better dye adsorption is obtained when the pH of the dye bath is on the acid side.

Next, examples will be given for further illustration of the present invention in detail.

EXAMPLE 1

A crepe de chine fabric composed of diacetate fiber, a cellulose acetate textile, was dipped in a dye bath of the following composition:

Kayacyl Sky Blue R (C.I. No. 62045).....	5% (O.W.F.).
$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_{12}\text{H}_{25}-\text{S} \\ \\ \text{C}_2\text{H}_5 \end{array} \right] + \text{Br}^-$	10% (O.W.F.).
Univadine W (a nonionic surfactant).....	5% (O.W.F.).
Bath ratio.....	1:50.

When the dyeing was carried out at 100° C. for 90 minutes, a product dyed to a bright deep shade was obtained. The wet fastness of the resulting dyed product was of a degree excelling that obtainable by disperse dyes.

EXAMPLE 2

A crepe de chine fabric composed of diacetate fiber was dipped in a dye bath of the following composition:

Nylomine Yellow AGS.....	4% (O.W.F.).
$\left[\text{C}_6\text{H}_5-\text{S}-\text{C}_6\text{H}_5 \right]^+\text{Br}^-$	10% (O.W.F.).
Univadine W.....	4% (O.W.F.).
Bath ratio.....	1:50.

The dyeing was carried out at 80° C. for 120 minutes. After completion of the dyeing of the fabric, it was washed in a bath containing an anionic surfactant, whereupon a product brightly dyed to a deep shade of yellow was obtained.

EXAMPLE 3

As a polyacrylonitrile fiber, "Kanekalon" was used. This fiber was dipped in a dye bath of the following composition:

Eriolin Red 2 BX (C.I. No. 26660).....	4% (O.W.F.).
$\left[\text{C}_{18}\text{H}_{37}-\text{S}-\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CH}_3 \end{array} \right]^+\text{Br}^-$	10% (O.W.F.).
Univadine W.....	4% (O.W.F.).
Bath ratio.....	1:50.

When the dyeing was carried out at 100° C. for 90 minutes, a product dyed to a deep shade of red was obtained.

EXAMPLE 4

Example 3 was repeated except that the dyeing was carried out at 110° C. for 90 minutes using "Orlon" instead of the "Kanekalon" used therein. A product dyed to a deep shade of red was obtained.

EXAMPLE 5

	Percent
Eriolin Red 2 BX (C.I. No. 26660).....	2
Liogen BC (trademark of Sandoz Company).....	5
$\left[\text{C}_{12}\text{H}_{25}-\text{S}-\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{C}_2\text{H}_5 \end{array} \right]^+\text{Br}^-$	10
Indalea ABV (12%).....	60
Methyl naphthalene (carrier).....	3
Water.....	20
Total.....	100

The modified polyester textile "Tetoron" T-89 was printed using a paste of the foregoing composition. After dyeing the textile, it was steamed at 120° C. for 90 minutes. This was followed by water-washing and laundering of the resulting dyed product to obtain a product dyed to a deep shade of red.

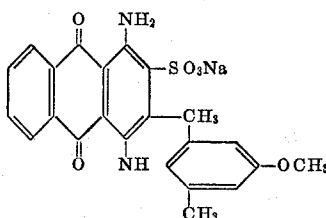
EXAMPLE 6

291 parts of dimethyl terephthalate, 207 parts of ethylene glycol, 29.1 parts of polyoxyethylene glycol (molecular weight about 1500), 0.102 part of calcium acetate monohydrate and 0.75 part of antimony trioxide were reacted in customary manner to obtain a copolymeric polyester having an intrinsic viscosity 0.45 and a softening point of 252.3° C. Fifty grams of this polyester and 10 grams of a polycaproamide of an intrinsic viscosity of 0.38 and a softening point of 213.7° C., both of which were rendered into particle size having maximum diameters 3-5 mm., were mixed together. The mixture was then charged to an autoclave which was reduced to a

pressure below 2 mm. Hg after having been purged with nitrogen. The temperature was then raised to 275° C. and by holding this temperature for 30 minutes the two polymers were thoroughly melted, followed by stirring for 30 minutes. The resulting blend had a softening point of 249.9° C. This polymer was spun and the resulting filaments were drawn in customary manner and a fiber (3.2 denier) having a tensile strength of 4.2 g./den. and an elongation of 38% was obtained. The dye adsorption was 86.4%.

The third component-contained modified polyester fiber obtained above was dipped in a dye bath of the following composition:

Xylene Fast Blue PR (C.I. Acid Blue 129).....	4% (O.W.F.).
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$\left[\text{C}_{12}\text{H}_{25}-\text{S}-\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \right]^+\text{Br}^-$	10% (O.W.F.).
Univadine W.....	4% (O.W.F.).
Bath ratio.....	1:50.

When the dyeing was carried out at 120° C. for 90 minutes, a product dyed brightly to a deep shade of blue was obtained.

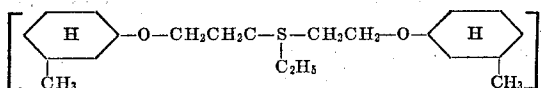
EXAMPLE 7

An autoclave was charged with 194 parts of dimethyl terephthalate, 138 parts of ethylene glycol, 194 parts of dihydroxypolyethylene oxide-propylene oxide block copolymer (average molecular weight about 1700, polyethylene oxide portion about 40 mol percent), 0.068 part of calcium acetate monohydrate and 0.50 part of antimony trioxide. The autoclave was then gradually heated while slowly introducing nitrogen. The temperature was raised to about 230° C. over a period of about 3 hours while distilling off the methanol formed as a result of the ester-interchange reaction. After the distillation off of the methanol was completed, 0.034 part of phosphoric acid was added as a stabilizer and the temperature was raised to 235° C. Stirring was carried out at atmospheric temperature for 30 minutes at this temperature, after which the pressure of the reaction system was reduced gradually to below 0.3 mm. Hg over a period of about 2 hours. The modified polyester had an intrinsic viscosity of 0.50 and a softening point of 258.1° C.

The modified polyester and a copolyamide prepared from caprolactam and hexamethylene diammonium terephthalate were both rendered into granular form having maximum particle diameters from 3 mm. to 5 mm. or less. Fifty parts of this modified polyester and 5 parts of the copolyamide were thoroughly mixed and charged to an autoclave. After purging the autoclave with nitrogen, its pressure was reduced to less than 0.2 mm. Hg and the temperature was raised to 275° C. This temperature was held for 30 minutes to thoroughly melt the two polymers, followed by stirring for 30 minutes. The resulting blend had a softening point of 255.4° C.

After vacuum drying this polymer at 100° C. for 5 hours, it was spun at 275° C. at a spinning speed of 500 meters per minute. The denier fineness of the resulting fiber drawn 4.5× at 80° C. was 2.8, and its tensile strength was 4.2 g./den. and elongation at break was 42%.

This fiber was dipped in a dye bath of the following composition:

Xylene Fast Blue PR (C.I. Acid Blue 129)	4% (O.W.F.).
	10% (O.W.F.).
Univadine W	3% (O.W.F.).
Bath ratio	1:50.

When the dyeing was carried out at 120° C. for 90 minutes, the fiber was dyed brightly to a deep shade of blue.

EXAMPLE 8

(a) Preparation of a polyamide-polyoxyalkylene glycol blend

Seventy-nine parts of caprolactam, 85 parts of hexamethylenediammonium terephthalate and 37 parts of polyoxyethylene glycol (average molecular weight about 8000) were dissolved in 40 parts of water and then charged to a polymerization vessel. After purging the vessel with nitrogen, it was slowly heated, the water distilling off being removed. The temperature of the remaining portion was raised to 270° C. and was stirred at this temperature for 60 minutes. This was followed by gradually reducing the pressure of the system to 0.77 mm. Hg at which pressure the polymerization reaction was carried out for 20 minutes. The $\eta_{sp./c.}$ of the resulting polyamide-polyoxyalkylene glycol blend was 1.02.

(b) Preparation of polyester

After charging an autoclave with 97 parts of dimethyl terephthalate, 69 parts of ethylene glycol, 0.034 part of calcium acetate monohydrate, 0.025 part of antimony trioxide and 0.009 part of cobalt acetate, it was slowly heated in a nitrogen atmosphere. The methanol which started to distill off in the neighborhood of 160° C. as a result of the ester-exchange reaction was removed to the outside of the system via a rectifying column.

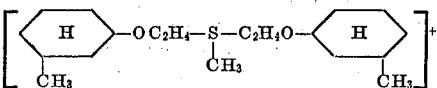
The temperature at the time of the completion of the distillation off of the methanol was 235° C. To the resulting prepolymer 0.07 part of trimethyl phosphate was added. The temperature of the system was raised to 280° C., stirring was carried out for 30 minutes and thereafter the pressure of the system was reduced to a high vacuum of below 0.2 mm. Hg over a period of 1½ hours. The $\eta_{sp./c.}$ of the resulting polyethylene terephthalate was 0.745.

(c) Preparation of polyester composition

Forty parts of the above prepared polyamide blend and 160 parts of polyethylene terephthalate were both dried and thereafter melted at 280° C. After blending the two together for 20 minutes in a nitrogen atmosphere, the system was reduced to a pressure below 0.5 mm. Hg where it was held for about 5 minutes to eliminate the low boiling components and thus obtain the polyester composition.

(d) Dyeing

The fiber obtained in customary manner by spinning the so obtained polyester composition following by drawing the resulting filaments was dipped in a dye bath of the following composition:

Xylene Fast Blue PR (C.I. Acid Blue 129)	4% (O.W.F.).
	10% (O.W.F.).
Actinol R-100 (primary polyoxyethylene lauryl ether)	1 g./liter.
Bath ratio	1:50.

It was possible to obtain products brightly dyed to deep shades of blue of Grade 9 using the above.

Further, when this fiber was dyed at 100° C. for 60 minutes in a dye bath of the following composition: disperse dye (C.I. Disperse Red 1 CI 1110) 4% (O.W.F.), Disper TL (Meisei Chemical Works Ltd.) 2 g./liter and acetic acid 4% (O.W.F.), and a bath ratio of 1:100, it was possible to dye the fiber to a deep shade of red. The TDI of this drawn fiber was 205° C.

Comparison 1

The case where conjoint use of an assistant is not used during the dyeing.

The polyester fiber obtained by the method of Example 8(a)(b)(c) was dipped in a dye bath of the following composition:

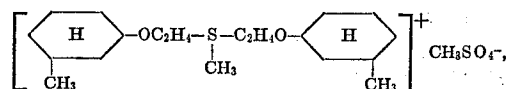
Acid dye (C.I. Acid Blue 129)	4% (O.W.F.).
Actinol R-100	1 g./liter.
Acetic acid	3% (O.W.F.).

When the dyeing was carried out at 120° C. for 90 minutes, the fiber was dyed to only a medium shade.

EXAMPLE 9

Twenty parts of a copolyamide ($\eta_{sp./c.}=0.54$) consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylene-diammonium terephthalate and 80 parts of polyethylene terephthalate ($\eta_{sp./c.}=1.05$) were melted at 285° C. under nitrogen for 10 minutes and blended. This blend was spun at 285° C. in customary manner. The freshly spun filaments were drawn 4.3× by means of an 85° C. pin, then shrunk at a temperature of 230° C. and again drawn 10% at a temperature of 150° C.

The fibers obtained were dyed using a dye bath composed of 4% (O.W.F.) of an acid dye Nylomin Blue GS (I.C.I.) (CI 62055), 5% (O.W.F.) of acetic acid, 4% (O.W.F.) of nonylphenoxypolyoxyethylene glycol and 4% (O.W.F.) of



and under the conditions of a bath ratio 1:100 and 120° C.×60 minutes, with the consequence that the fiber was dyed to a deep blue shade (Grade 8-9).

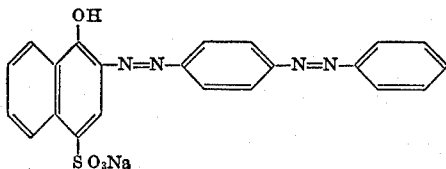
EXAMPLE 10

Thirteen parts of polyhexamethylene adipamide

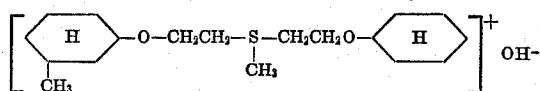
($\eta_{sp./c.}=0.63$)

and 87 parts of polyethylene terephthalate ($\eta_{sp./c.}=1.05$) were melt-blended as in Example 9, after which the resulting blend was melt-spun at 285° C. in customary manner. The freshly spun filaments were drawn 4.25× by means of an 87° C. pin, then shrunk 30% at a temperature of 215° C. and thereafter again drawn 15% at a temperature of 160° C.

This fiber was dyed using a dye bath composed of 4% (O.W.F.) of Eriodin Red 2BX CI No. 26660 of the formula



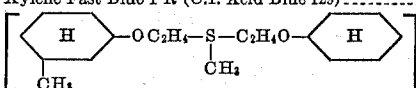
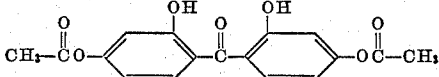
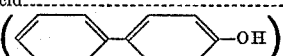
5% (O.W.F.) of acetic acid, 4% (O.W.F.) of nonylphenoxypolyethylene glycol and 4% (O.W.F.) of



and under the conditions of a bath ratio 1:100 and 120° C. x 60 minutes, thereby obtaining a product dyed to a deep red shade (Grade 8-9).

EXAMPLE 11

"Tetoron" T-89 (a polyester fiber) was dyed at 130° C. for 90 minutes in a dye bath of the following composition:

Xylene Fast Blue PR (C.I. Acid Blue 129).....	1% (O.W.F.).
	1% (O.W.F.).
	2% (O.W.F.).
Acetic acid.....	2% (O.W.F.).
P.P.P. ().....	20% (O.W.F.).
Bath ratio.....	1:100.

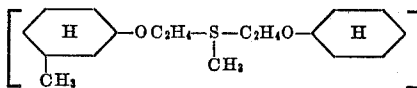
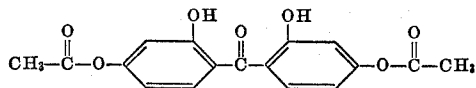
When soaping was carried out for 30 minutes at 60° C. in a 0.2% solution of Scourol after completion of the dyeing operation, a product dyed to a bright shade of blue was obtained. When this dyed product was exposed for 40 hours in a Fade-Ometer, no fading was observed at all. When, as a control, a specimen dyed in a dye bath of the above composition but from which the 2,2'-dihydroxy-4,4'-diacetylbenzophenone was eliminated, was similarly exposed for 40 hours in a Fade-Ometer, marked fading occurred.

EXAMPLE 12

Twenty parts of a copolyamide ($\eta_{sp./c.}=0.54$) consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium terephthalate were melt-blended with 80 parts of polyethylene terephthalate ($\eta_{sp./c.}=0.63$) for 10 minutes at 285° C. under nitrogen, after which the resulting blend was spun in customary manner at a spinning temperature of 285° C. The freshly spun filaments were drawn 4.3x by means of an 85° C. pin, then shrunk 25% at a temperature of 230° C. and thereafter again drawn 10% at a temperature of 150° C.

The fibers obtained were dipped in a dye bath of the composition below:

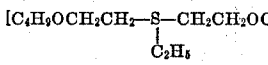
The dyeing was carried out at 120° C. for 90 minutes. After completion of the dyeing operation, soaping of the dyed fiber was carried out for 30 minutes at 50° C. in a 0.2% solution of Marseilles soap. As a result, a product dyed to a bright shade of blue was obtained. Although this dyed product was exposed for 40 hours in a Fade-Ometer, there was no fading at all. When, as a control, a specimen dyed in a dye of the above composition

Xylene Brilliant Blue 5 GM.....	4% (O.W.F.).
	4% (O.W.F.).
2,2-dihydroxy-4,4'-diacetylbenzophenone.....	4% (O.W.F.).
	
Acetic acid.....	3% (O.W.F.).
Bath ratio.....	1:50.

tion but from which 2,2'-dihydroxy-4,4'-diacetylbenzophenone was eliminated was similarly exposed for 40 hours in a Fade-Ometer, marked fading was noted.

EXAMPLE 13

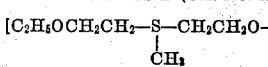
The polyvinyl chloride fiber "Valren" was dipped in a dye bath of the following composition:

Xylene Fast Blue PR (C.I. Acid Blue 129).....	2% (O.W.F.).
	5% (O.W.F.).
Univadine W.....	2% (O.W.F.).
Bath ratio.....	1:50.

The temperature of the bath was then slowly raised and the dyeing was carried out at 100° C. for 60 minutes, whereupon a product brightly dyed to a deep shade (Grade 8-9) of blue was obtained. The colorfastness to light and washing of the resulting dyed product was very excellent. The dye adsorption was 80%.

EXAMPLE 14

The polyvinyl chloride fiber "Valren" was dipped in a dye bath of the following composition:

Suminol Fast Red B (C.I. No. 14680).....	3% (O.W.F.).
	3% (O.W.F.).
Univadine W.....	2% (O.W.F.).
Bath ratio.....	1:50.

The temperature of the bath was then slowly raised and the dyeing was carried out at 100° C. for 60 minutes to yield a product dyed to a bright deep shade (Grade 8-9) of blue. The colorfastness to light and washing of the so obtained product was very outstanding. The dye adsorption was 80%.

15 EXAMPLE 15

The polyvinyl chloride fiber "Valren" was dipped in a dye bath of the following composition:

Suminol Fast Red B (C.I. No. 14680).....	3% (O.W.F.).
$[C_2H_5OCH_2CH_2-\underset{\substack{ \\ CH_3}}{S}-CH_2CH_2O-C_2H_5]+CH_3SO_4^-$	3% (O.W.F.).
Trichlorobenzene (carrier).....	3 g./liter.
Univaine W.....	2 g./liter.
Bath ratio.....	1:50

The temperature of the bath was slowly raised and the dyeing was carried out at 90° C. for 60 minutes, whereupon a product dyed to a bright shade (Grade 9-10) of red was obtained. The dye adsorption was 95%.

EXAMPLE 16

The dyeing was carried out at 60° C. for 60 minutes as in Example 14, except that the polyvinyl chloride fiber "Tevilon" was used instead of "Valren." A product dyed to a bright shade of red was obtained.

EXAMPLE 17

The dyeing was carried out at 100° C. for 60 minutes as in Example 14 except that a metal-containing dye-stuff "Kayakalan Red 2BL" was used instead of the dye-stuff used in Example 14, with the result that a product dyed to a deep shade of red was obtained.

EXAMPLE 18

The dyeing was carried out at 90° C. for 60 minutes as in Example 15, except that instead of the dyestuff used therein a reactive dye Remasole Red B was used, with the result that a product dyed to a deep shade of red was obtained.

EXAMPLE 19

A crepe de chine fabric composed of diacetate fiber, a cellulose acetate textile, was dipped in a dye bath of the following composition:

Kayacyl Sky Blue R (C.I. No. 62045)	5% (O.W.F.).
$\left[\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{S}}-\text{CH}_2\text{CH}_2\text{O}-\text{C}_4\text{H}_9 \right]_n \text{C}_2\text{H}_5\text{S O}_4^-$	
Univadine W	5% (O.W.F.).
Bath ratio	1:50.

As a result, a product dyed to a deep shade of blue was obtained.

EXAMPLE 20

A mixed woven fabric composed of 6 nylon and diacetate fibers was dipped in a dye bath of the following composition:

Kayacyl Sky Blue R (C.I. No. 62045)	4% (O.W.F.).
$\left[\text{C}_6\text{H}_4\text{--OCH}_2\text{CH}_2\text{--}\underset{\text{CH}_3}{\text{S}}\text{--CH}_2\text{CH}_2\text{O--C}_6\text{H}_4 \right]^+\text{CH}_3\text{SO}_4^-$	10% (O.W.F.).
Univadine W	4% (O.W.F.).
Soda Ash	1 g./liter.
Bath ratio	1:50.

When the dyeing was carried out at 100° C. for 90 minutes, a product dyed to a bright shade of blue and being excellent in solid dyeing property was obtained.

16
EXAMPLE 21

	Percent
Kayacyl Sky Blue R (C.I. No. 62045).....	2
Thiodiethylene glycol.....	2
5 $\left[\begin{array}{c} \text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2\text{OC}_4\text{H}_9 \\ \text{C}_2\text{H}_5 \end{array} \right]_v + \text{C}_2\text{H}_5\text{SO}_4^-$	4
Indalca ABV (12%) (a paste consisting predominately of locust bean gum).....	70
10 Water.....	22
Total.....	100

15 A crepe de chine fabric of diacetate fiber was printed using a paste of the foregoing composition. After drying the printed fabric, it was steamed at 100° C. for 40 minutes. The so obtained dyed fabric was then water-washed and laundered, whereupon a product which was dyed to a deep shade of blue was obtained.

EXAMPLE 22

The modified polyester fiber "Tetoron" T-89 was dipped in a dye bath of the following composition:

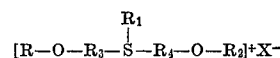
	Lissamine Fast Violet 2 BS (C.I. No. 62020).....	4% (O.W.F.).
25	$\left[\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{S}}-\text{CH}_2\text{CH}_2\text{OC}_4\text{H}_9 \right]^+ \text{C}_2\text{H}_5\text{SO}_4^-$	10% (O.W.F.).
	Univadine W.....	4% (O.W.F.).
	Sulfuric acid.....	1 g./liter.

When the dyeing was carried out at 120° C. for 2 hours, a product dyed to a deep shade of violet was obtained.

What is claimed is:

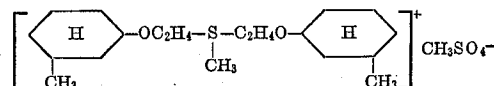
35 1. A method of dyeing a textile fiber selected from the group consisting of modified polyester, polyvinyl chloride, polyacrylonitrile, and cellulose acetate fibers, which comprises dyeing the fibers with an anionic dyestuff in the presence of at least one compound selected from sulfonium salts of the formula

40

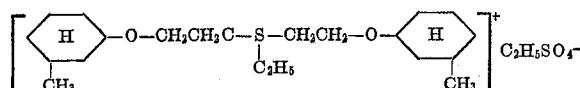


wherein R, R₁ and R₂ are each selected from the group
45 consisting of alkyl, alkenyl, cycloalkyl, aryl and aralkyl
groups of 1-18 carbon atoms, R₃ and R₄ are each alkyl
groups of 1-5 carbon atoms and X is selected from the
group consisting of halogens, alkoxy sulfate and OH
group.

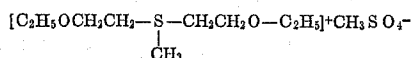
2. The method of claim 1 wherein said sulfonium salt is



3. The method of claim 1 wherein said sulfonium salt is



4. The method of claim 1 wherein the sulfonium salt is



5. The method of claim 4 wherein the textile fiber is a modified polyester selected from the group consisting of:

- (a) that obtained by melt-spinning a blended composition of 60 to 99.5% by weight of polyester and 40 to 0.5% by weight of polyamide and drawing the resulting filaments; (b) that obtained by melt-spinning a blended composition of 40 to 0.5% by weight of polyamide with 60 to 99.5% by weight of a copolyester obtained by copolymerizing with a polyester 1 to 30% by weight, based on the overall weight of the composition, of a polyoxyalkylene glycol, and drawing the resulting filaments; (c) that obtained by melt-spinning a blended composition of 99.5 to 60% by weight of polyester and 0.5 to 40% by weight of a polyamide blend containing, based on the overall weight of the composition, 1 to 30% by weight of a polyoxyalkylene glycol, and drawing the resulting filaments; (d) that obtained by melt spinning a blended composition of 60 to 99.5% by weight of polyester, 0.5 to 40% by weight of polyamide and 0.6 to 30% by weight of polyoxyalkylene glycol and drawing the resulting filaments; (e) that obtained by melt-spinning a blended composition of 60 to 99.5% by weight of polyester and 40 to 0.5% by weight of polyamide, drawing the resulting filaments, followed by heat treating and shrinking the filaments, and thereafter again drawing the filaments; (f) that ob-

tained by melt-spinning a blended composition of 60 to 99.5% by weight of polyester and 40 to 0.5% by weight of polyamide, drawing the resulting filaments, followed by shrinking the filaments 2% to 50% of their initial length by heating the filaments at a temperature within the range of 140° C. and the melting temperature of said polyester filaments and thereafter redrawing the filaments; and (g) that obtained by melt-spinning a blended composition of 60 to 99.5% by weight of polyester and 40 to 0.5% by weight of polyamide, drawing the resulting filaments, followed by heat treating and shrinking the filaments, and thereafter again drawing said filaments at a rate of elongation ranging from 2% of their initial length to the point at which breakage of said polyester filaments takes place, at a temperature within the range of room temperature and 230° C.

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THOMAS J. HERBERT, JR., Primary Examiner

U.S. Cl. X.R.

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