United States Patent Office 3,666,403
Patented May 30, 1972

3,666,403

PROCESS FOR DYEING MODIFIED POLYESTER FIBERS IN THE PRESENCE OF QUATERNARY AMMONIUM SALTS

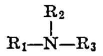
Shiro Shimauchi, Takatsuki-shi, Osaka-fu, Norihiro Minemura, Takeshi Matsui, and Kenji Ito, Ibaraki-shi, Osaka-fu, and Takue Shima, Shoji Kawase, and Masataka Oshima, Yamaguchi-ken, Japan, assignors to Teijin Limited, Osaka, Japan

No Drawing. Filed Mar. 4, 1969, Ser. No. 804,294
Claims priority, application Japan, Mar. 14, 1968, 43/16,906; Apr. 5, 1968, 43/22,510; June 3, 1968, 43/56,828; July 19, 1968, 43/51,277; July 30, 1968, 43/54,071; Aug. 22, 1968, 43/60,034; Aug. 23, 1968, 43/60,356; Aug. 28, 1968, 43/61,638; Sept. 26, 1968, 43/69,736
Int. Cl. D06p *5/06*
U.S. Cl. 8—172 **3 Claims**

ABSTRACT OF THE DISCLOSURE

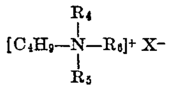
A method of dyeing a textile fiber selected from the group consisting of the modified polyester, polyvinyl chloride, acrylonitrile and cellulose acetate fibers, said method comprising dyeing said fiber with an anionic dyestuff in the presence of at least one compound selected from the group consisting of specific tertiary amines, quaternary ammonium salts, sulfonium salts, tertiary phosphines, and quaternary phosphonium salts.

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



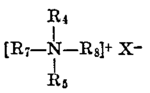
$$R_1-\overset{R_2}{\overset{|}{N}}-R_3 \qquad \text{(I)}$$

wherein R_1 and R_2 are each selected from the group consisting of alkyl and alkenyl groups of 3–5 carbon atoms, and R_3 is selected from the group consisting of alkyl, alkenyl, cycloalkyl, aryl and aralkyl groups of 1–18 carbon atoms; the quaternary ammonium salts of the formula



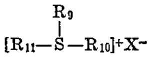
$$[C_4H_9-\overset{R_4}{\underset{R_5}{N}}-R_6]^+X^- \qquad \text{(II)}$$

wherein R_4 and R_5 are each selected from the group consisting alkyl and alkenyl groups of 1–5 carbon atoms and their derivatives, R_6 is selected from the group consisting of alkyl and alkenyl groups of 1–18 carbon atoms and their derivatives, and X is selected from the group consisting of halogens, alkyl sulfuric acid residues and OH group; the quaternary ammonium salts of the formula



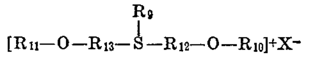
$$[R_7-\overset{R_4}{\underset{R_5}{N}}-R_8]^+X^- \qquad \text{(III)}$$

wherein R_4 and R_5 are as above defined, R_7 is selected from the group consisting of alkyl and alkenyl groups having 5–18 carbon atoms and their derivatives, R_8 is selected from the group consisting of phenyl, benzyl, naphthyl, alpha-naphthylmethyl, diphenyl and cycloalkyl groups having a substituent, and X is as above defined; the sulfonium salts of the formula



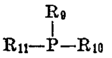
$$[R_{11}-\overset{R_9}{\overset{|}{S}}-R_{10}]^+X^- \qquad \text{(IV)}$$

wherein R_9, R_{10} and R_{11} are each selected from the group consisting of alkyl, alkenyl, cycloalkyl, aryl and aralkyl groups of 1–18 carbon atoms and their derivatives, and X is as above defined; the sulfonium salts of the formula



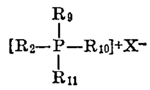
$$[R_{11}-O-R_{13}-\overset{R_9}{\overset{|}{S}}-R_{12}-O-R_{10}]^+X^- \qquad \text{(V)}$$

wherein R_9, R_{10}, R_{11} and X are as above defined, and R_{12} and R_{13} are each alkyl group of 1–5 carbon atoms; the tertiary phosphines of the formula



$$R_{11}-\overset{R_9}{\overset{|}{P}}-R_{10} \qquad \text{(VI)}$$

wherein R_9, R_{10} and R_{11} are as above defined; and the quaternary phosphonium salts of the formula



$$[R_2-\overset{R_9}{\underset{R_{11}}{P}}-R_{10}]^+X^- \qquad \text{(VII)}$$

wherein R_2, R_9, R_{10}, R_{11} and X have the same significance as above.

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

Numerous methods of dyeing polyvinyl chloride fiber 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, but none of the conventional methods have been able to provide dyed products which are fully deep in shade. Therefore, a second object of the invention is to provide a dyeing method by which the polyvinyl chloride fiber can be dyed to fully satisfactory deep shades.

The acrylonitrile fiber is usually dyes with the cationic dyestuffs. However, in this case also, when expansion of the scope of color and case of dyeing of mixed spun products are considered, the impartation of dyeability by means of the acid dyes is to be desired. 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 acrylonitrile fiber as well as facilitates the dyeing of mixed spun products, especially the mixed spun products with wool.

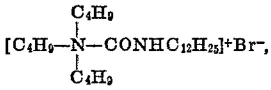
The cellulose acetate fiber is also dyed with the disperse dyes as in the case with the polyester fiber, but in this case also there was noted the shortcoming that the brightness of the dyed product was not yet fully satisfactory. A fourth object is therefore to provide a dyeing method which can impart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

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

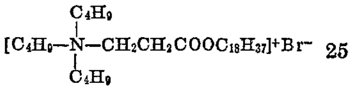
We furthered our researches from both aspects of the modification of the polyester fiber and the method of dyeing the same. As a consequence, we found that shaped articles of certain classes of modified polyesters could be dyed to exceedingly deep shades when dyed by the anionic dyestuffs in the presence of at least one of the compounds having a specific structure as indicated by the hereinbefore given Formulas I–VII.

The tertiary amines to be used in the present invention are those having the hereinbefore indicated Formula I. Included as tertiary amines are such, for example, as tributylamine, monopropyl - dibutylamine, monoethyl-dibutylamine, monoallyl-dibutylamine, monoamyl-dibutylamine, tripropylamine, triamylamine, N,N-dibutylaniline and dibutylbenzylamine.

On the other hand, the quaternary ammonium salts to be used in this invention are those having the hereinbefore indicated Formula II. As specific compounds of this formula, mention can be made of such, for example, as tetrabutylammonium chloride, tributyllaurylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium hydroxide, tributylallylammonium bromide, butyldimethyllaurylammonium bromide, tributyloleilammonium bromide, butyldiethyllauryl bromide, tributylmethylammonium methosulfate, tributylamylammonium bromide, tributyl-stearylammonium bromide, butyldiethanollaurylammonium hydroxide.

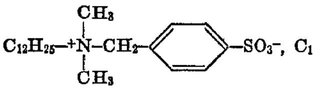


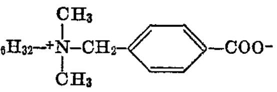
$$[C_4H_9-\overset{\displaystyle C_4H_9}{\underset{\displaystyle C_4H_9}{N}}-CONHC_{12}H_{25}]^+Br^-,$$



$$[C_4H_9-\overset{\displaystyle C_4H_9}{\underset{\displaystyle C_4H_9}{N}}-CH_2CH_2COOC_{18}H_{37}]^+Br^-$$

and tributylpropanolammonium bromide. On the other hand, the one other class of quaternary ammonium salts that are used in the present invention are those having the hereinbefore indicated Formula III. Specific compounds of this formula include such, for example, as dimethyllauryl-2-chlorobenzylammonium chloride, diethylstearyl 2-chlorobenzylammonium bromide, dimethylstearyl 2-nitrobenzylammonium chloride, dimethyllauryl 3,4-dichlorobenzylammonium chloride, dipropyllauryl 4-chloronaphthylmethylammonium iodide, ethylmethyloleil 4-methoxybenzylammonium iodide, diethylpalmityl 3,4-dichlorobenzylammonium chloride,





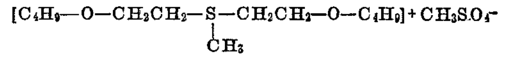
n-oleyldimethyl 2-nitrobenzylammonium chloride, n-stearyldimethyl 4-methylbenzylammonium chloride and n-lauryldimethyl 4-methylphenylammonium chloride. These compounds can be used either alone or in combinations of two or more classes.

The sulfonium salts to be used in the present invention are compounds having the hereinbefore indicated Formula IV. As specific compounds, in the case, for example, where R_9, R_{10} and R_{11} of the foregoing formula are saturated hydrocarbon residues, included are such as the dimethylstearylsulfonium salt, methylethyllaurylsulfonium salt, methylpropyllaurylsulfonium salt, methylbutyllaurylsulfonium salt, ethylpropylstearylsulfonium salt, tributylsulfonium salt, dibutylpropylsulfonium salt and diethylcyclohexylsulfonium salt.

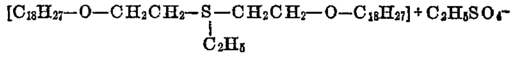
On the other hand, as examples of unsaturated hydrocarbon residues, there are the alkenyl or the aryl or aralkyl groups such as phenyl, benzyl, naphthyl and naphthylmethyl. For example, mention can be made of such as the dimethylbenzylsulfonium salt, diethylbenzylsulfonium salt, dibutylbenzylsulfonium salt, methylethylnaphthylsulfonium salt, ethylaryllaurylsulfonium salt, methylbutyloleilsulfonium salt, ethylpropylphenylsulfonium salt and diarylmethylsulfonium salt. Further as derivatives of saturated or unsaturated hydrocarbon residues, useable are those hydrocarbon residues having substituents on their side or straight chain. The substituents include such as alkyl, aryl, alkenyl, nitro, alkoxy, halogens, cyancarboxy and sulfonic acid. Needless to say, the substituents are not restricted to those mentioned. As these derivatives, included are such, for example, as dimethyl 4-chlorobenzylsulfonium salt, 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 V.

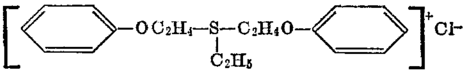
As specific compounds, included in this case are such, for example, as follows:

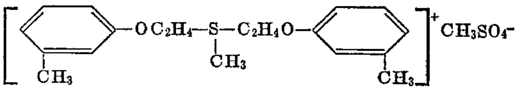


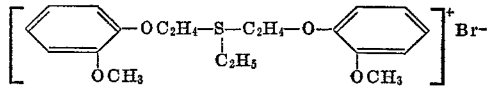
$$[C_4H_9-O-CH_2CH_2-\underset{\displaystyle CH_3}{S}-CH_2CH_2-O-C_4H_9]^+CH_3SO_4^-$$

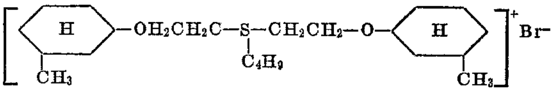


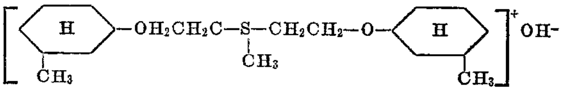
$$[C_{18}H_{27}-O-CH_2CH_2-\underset{\displaystyle C_2H_5}{S}-CH_2CH_2-O-C_{18}H_{27}]^+C_2H_5SO_4^-$$

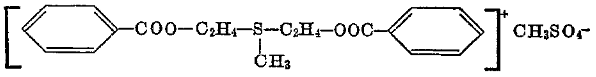












The tertiary phosphines to be used in the present invention are those of the hereinbefore indicated Formula VI. As specific compounds, mention can be made of such, for example, as tributylphosphine, triphenylphosphine, lauryldimethylphosphine, triethylphosphine, lauryldibutylphosphine, diphenylbutylphosphine, dibutylallylphosphine and diethyloleilphosphine.

On the other hand, the quaternary phosphonium salts to be used in this invention are those having the hereinbefore indicated Formula VII. As specific compounds, included are such, for example, as the following:

$[(C_6H_5)_4P]^+\ Br^-$

$[(C_6H_5)_4P]^+\ Cl^-$

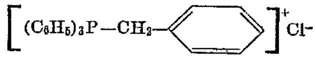
$[(C_2H_5)_4P]^+\ OH^-$

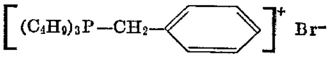
$[(C_4H_9)_4P]^+\ OH^-$

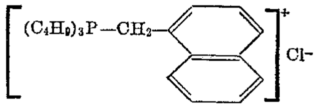
$[(C_6H_5)_3P-C_2H_5]^+\ Br^-$

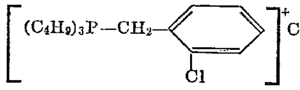
$[(C_2H_5)_3P-CH_2-H]^+\ I^-$

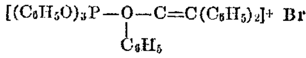
$[(C_6H_5)_3P-C_4H_9]^+\ Br^-$



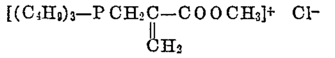




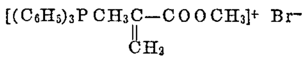




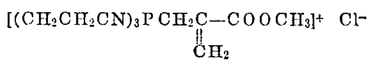
$$[(C_6H_5O)_3P-\underset{\displaystyle C_6H_5}{O}-C=C(C_6H_5)_2]^+\ Br^-$$



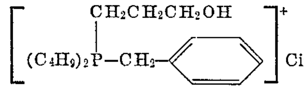
$[(C_4H_9)_3{-}PCH_2\underset{\underset{CH_2}{\|}}{C}{-}COOCH_3]^+\ Cl^-$

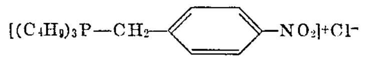


$[(C_6H_5)_3PCH_3\underset{\underset{CH_3}{\|}}{C}{-}COOCH_3]^+\ Br^-$



$[(CH_2CH_2CN)_3PCH_2\underset{\underset{CH_2}{\|}}{C}{-}COOCH_3]^+\ Cl^-$





$[(C_4H_9)_3P{-}CH_2CHCH_2]^+Br^-$

The aforementioned sulfonium, quaternary ammonium and quaternary phosphonium salts are especially characterized by their cationic property, there being little, if any, difference in their effects that results due to differences in their anions. Further, it is possible to use two or more of these classes in combination. Again, the aforesaid cationic compounds (sulfonium, ammonium and phosphonium salts) may also be such cationic compounds as amphoteric surfactants.

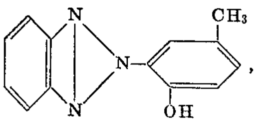
Polyester, as used herein, is principally intended to be polyethylene terephthalate. However, it also refers to those polyesters which comprise at least 60 mol percent of ethylene terephthalate units and in which a part of the acid or dihydroxy component is substituted by one or more classes of either 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-bishydroxyethoxybenzene, bisphenol A and compounds having the tertiary amino group [e.g. butyl-di(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 pentaerythitol and trimesic acid are copolymerized to a certain extent with substantial crosslinkings will also do. 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 compositions," as used herein, refer 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 polyalkylene glycol with polyester, the blended composition of polyester and a polyamide blended containing a polyalkylene glycol, and the blended composition of polyester, polyamide and polyalkylene glycol. Modified polyester fibers which are particularly desirable include: (a) that obtained by melt-spinning a blended composition of 60–99.5 wt. percent of polyester and 40–0.5 wt. percent of polyamide and drawing the resulting filaments; (b) that obtained by melt-spinning a blended composition of 40–0.5 wt. percent of polyamide with 60–99.5 wt. percent of a copolyester obtained by copolymerizing with a polyester 1–30 wt. percent, based on the overall weight of the composition, of a polyalkylene glycol and drawing the resulting filaments; (c) that obtained by melt-spinning a blended composition of 99.5–60 wt. percent of polyester 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) that obtained by melt-spinning a blended composition consisting of 60–99.5 wt. percent of polyester, 0.5–40 wt. percent of polyamide and 0.6–30 wt. percent of polyalkylene glycol and drawing the resulting filaments; (e) that obtained by melt-spinning a blended composition of 60–99.5 wt. percent of polyester and 40–0.5 wt. percent of polyamide and drawing the resulting filaments, then shrinking the filaments by heat treating them and thereafter redrawing the filaments; (f) that obtained by melt-spinning a blended composition of 60–99.5 wt. percent of polyester and 40–0.5 wt. percent of 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 said polyester fiber and thereafter redrawing the filaments; and (g) that obtained by melt-spinning a blended composition of 60–99.5 wt. percent of polyester and 40–0.5 wt. percent of polyamide and drawing the resulting filaments, followed by shrinking the filaments by heat treating them and thereafter redrawing said 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 said polyester fiber takes place.

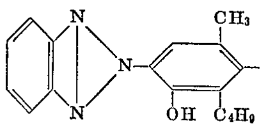
The manufacture of a fiber by melt-spinning and drawing a blended composition of polyester and some amount of polyamide is known (British patent specification No. 610,140). However, the fiber which has been merely melt-spun and drawn in this manner does not demonstrate desirable dyeability when the usual method of dyeing it with anionic dyestuffs is employed. And it is only when the fiber is dyed by the invention dyeing method that it is possible to provide products dyed to bright and of deep shades and which are thus useful. Now, as a result of our further researches with a view to improving on the dyeability of the fiber itself that is obtained from the polyester-polyamide composition, we found that when one of the methods comprehended by 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 said 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 of the compounds selected from the previously described compounds of Formulas I–VII, dyed products which were of greater brightness and of deeper shades could be obtained. Hence, 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 invention dyeing method for improving the light fastness of the dyed products. The following compounds can be used as ultraviolet absorbents in the present invention.

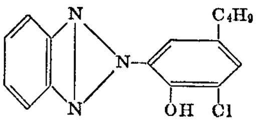
(1) 2-(2'-hydroxyphenyl)benzotriazole series, for example, those such as follows:



,

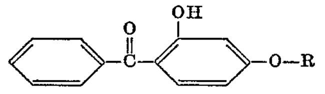


and

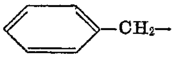


(2) 2-hydroxybenzophenone series, for example, those of the following formulas:

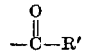
(a)



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



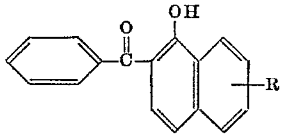
or



$-\overset{O}{\overset{\|}{C}}-R'$

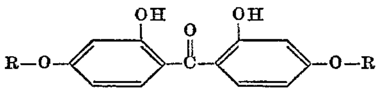
where R′ is alkyl or aryl); and

(b)

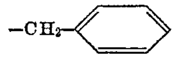


wherein R is H or $-SO_3H$.

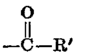
(3) 2,2′-dihydroxybenzophenone series, for example, those of the formula



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



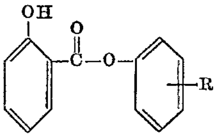
or



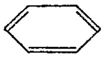
$-\overset{O}{\overset{\|}{C}}-R'$

(where R is alkyl or aryl).

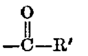
(4) Phenylsalicylic acid series, for example, those of the formula



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



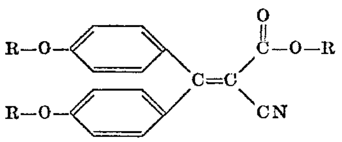
or

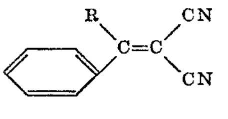


$-\overset{O}{\overset{\|}{C}}-R'$

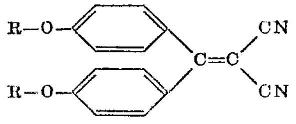
(where R′ is alkyl or aryl).

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





and



wherein R is alkyl or aryl.

While the amount used of these ultraviolet absorbents will vary depending upon such as the class of the material to be dyed, the class of the dyestuff and the concentration and bath ratio, the use of about 1–10% (O.W.F.) of the material to be dyed will do. It is also possible to achieve the end 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 such as the inorganic acids as sulfuric and acetic acids and the salts thereof; and benzenesulfonic acid, toluene-sulfonic acid, higher alkyl benzene sulfonic 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 such as their thermal resistance, etc. Mention can be made of such, for example, as polycaproamide, polyenanthamide, 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 these polyamides, the aromatic polyamides such, for example, as that which has copolymerized therewith the hexamethylene - diammonium terephthalate component gives especailly desirable results with respect to such as 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 polyamide exceeds 40% by weight, the properties as a polyester fiber are lost. Hence, it is undesirable for the content of the polyamide to be without the range indicated above.

In addition, the dyeability of the fiber can be further enhanced by the incorporation in the foregoing polyesters and/or polyamides in an amount not exceeding 30% by weight, based on the overall weight of the fiber, of a polyoxyalkylene glycol. As the polyoxyalkylene glycols, mention can be made of such, for example, as polyoxyethylene glycol, polyoxypropylene glycol, polyoxyethylene-oxypropylene glycol block or random copolymer, methoxypolyoxyethylene glycol, phenoxypolyoxyethylene glycol and octylphenoxypolyoxyethlene glycol. These poloxyalkylene 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 after-chlorinated 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 acrylonitrile fibers to be used in the present invention, useable are the acrylic fibers that do not possess dye receptive sites. That is to say, included are Orlon (trademark of Du Pont Company) type, Dynel (trademark of Union Carbide and Chemical Company) type, and the acrylic conjugated fiber. Again, it goes with out saying that the present invention has applicability to also 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 fiber obtained by the after acetylation technique. Again, the invention can, of course, be applied to the mixed textile products of the foregoing fiber with the other classes of fibers. The invention method is especially effective in the case of mixed product of the acetate fiber with the polyamide fiber, since both fibers are dyeable with acid dyes.

Now, the modified polyester fibers that can be dyed by means of the invention method are those 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 here used, 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 a 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), followed 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 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 number being used.

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

wherein

d_o=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 invention method is used.

Now, if the present invention is applied to polyamide fibers (e.g. nylon) the results become 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 become negative to result in the decline in the dye adsorption.

Further, the anionic dyestuffs, as referred to herein, denote all of the 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 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 such 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 conjointly the known carriers. 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 the polyvinyl chloride fiber, 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 conjointly the known carriers.

Further, in the case of the cellulose acetate and acrylonitrile fibers, the amount used of the aforesaid compounds 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, carriers dyeing is also effectively carried out by conjointly using the 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.

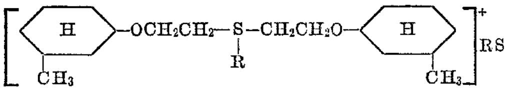
For carrying out the dyeing levelly by dispersing the dye-stuff thoroughly and for preventing the formation of tar, it is prefered to use a suitable nonionic surfactant in the invention method. Surfactants such as indicated are those which are usually widely used as dispersants. Included are, for example,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

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

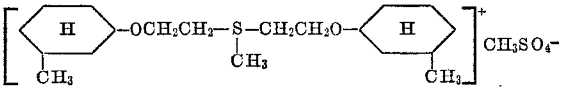
While the particulars of the principle underlying the invention method are not clear, it is believed that the water dissolved or dispersed dyestuff forms a complex with the aforesaid compounds of Formulas I–VII to become possessed with compatibility and affinity with respect to the hydrophobic fibers and simultaneously to function at times as carrier at elevated temperature to become diffused into the interior of the fiber and result in the adsorption of the dye. Hence, the balance of the affinity between the dyestuff and the aforesaid compounds of Formulas I–VII 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 only those cases where the specific compounds defined by the foregoing formulas are used. Hence, the compounds most suitable differ depending upon the fibers to which application of the invention is made.

As regards the polyvinyl chloride and polyacrylonitrile fibers, the compounds having the Formulas I, II, IV, V, VI and VII are suitable of the aforesaid compounds of Formulas I–VII. An of these, as the compounds of Formula I, tributylamine, triamylamine and dibutylamine are especially desirable. As the compounds of

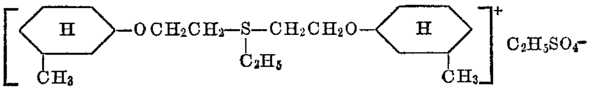
Formula VI, the effects are great in the case of tributylphosphine and triphenylphosphine. In using the compounds of Formuas I and VI, it is preferred from the standpoint of dye adsorption that the pH of the dye bath is not greater than 5. Of the compounds having the Formula II, those having the tributyl group are especially desirable from the standpoint of dye adsorption. Preferably used are, for example, the tetrabutylammonium salts and tributyllaurylammonium salts. Of the sulfonium salts of Formulas IV and V, the use of especially the tributylsulfonium salts and the



type is preferred. For example, the use of tributylsulfonium chloride,



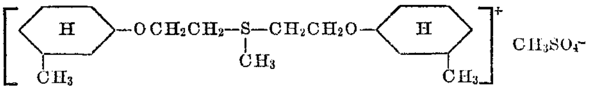
and



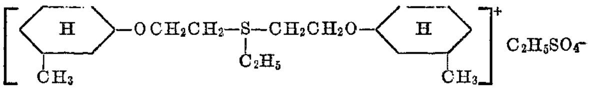
is to be desired. The cationic property of all of the compounds of Formula VII is great and hence they are suitable, particularly desirable being the tributylbenzylphosphonium salts, tetrabutylphosphonium salts and triphenylphosphonium salts.

In the case of the cellulose acetate fiber, the compounds of Formulas I, II, IV and VII of the compounds of Formulas I–VII are especially suitable. Of these, as compounds of Formula I, tributylamine, triamylamine and N,N-dibutylaniline can be mentioned. As compounds of Formula II, those having the tributyl group are satisfactory as regards dye adsorption. These are exemplified by such as tetrabutylammonium salts, tributyllaurylammonium salts, tributylstearylammonium salts and tributylallylammonium salts. As compounds of Formula IV, mention can be made of the tributylsulfonium salts. On the other hand, as compounds of Formula VII, included are those having the tributyl group such as tributylbenzylammonium salts and tributylallylphosphonium salts. or triphenylbutylphosphonium salts.

In the case of the modified polyester fibers, very satisfactory dye adsorption is obtained regardless of which type of the compounds of Formulas I–VII is used. As compounds which are especially satisfactory, included are such, for example as: tributylamine, triamylamine, N,N-dibutylamine, tributylphosphine, triphenylphosphine, tributylmethylammonium methosulfate, tributyllaurylammonium salts, tetrabutylammonium salts, tributylpropanolammonium salts, lauryldimethyl 2-chlorobenzylammonium salts, stearyldiethyl 2-chlorobenzylammonium salts, lauryldiethyl 2-nitrobenzylammonium salts, tributylbenzylphosphonium salts, tetrabutylphosphonium salts, triphenylbenzylphosphonium salts, triphenylbutylphosphonium salts, tributylarylphosphonium salts, tributylsulfonium salts,



and



In the case of the tertiary amines and phosphines, 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. In the examples $\eta_{sp/c}$ indicates the specific viscosity measured at 35° C. using orthochlorophenol as the solvent and intrinsic viscosity is defined as

$$\lim_{c \to 0} \frac{\eta_{sp}}{c}$$

in which c is concentration in grams of polymer per 100 cc. of solution. Also all the parts are on a weight basis. As to dyeability, it was indicated by the rate of dye adsorption in the case disperse dyes, and in the case of ionic dyes it was indicated by a qualitative indication, rate of dye adsorption and classification into grades ranging from 1 to 10. Grade 1 denotes that no dyeing at all took place, while Grades 2 and higher denote that as the grade becomes higher, the dyeing becomes better. Dyeings which are of practical use are those having ratings of Grade 5 or higher.

On the other hand, TDI denotes the decomposition initiating temperature which has been measured in air at the rate of a temperature rise of 10° C. per minute using the differential heat analyzer.

EXAMPLE 1

An autoclave was charged with 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, after which the autoclave was gradually heated while slowly introducing nitrogen. The temperature was raised to 230° C. over a period of about 3⅓ hours while distilling off the methanol formed as a result of the ester-interchange reaction. After completion of the distillation off of the methanol, 0.051 part of phosphoric acid was added and the temperature was raised to 275° C. After stirring for 30 minutes at atmospheric pressure at this temperature, the pressure of the reaction system was gradually reduced to less than 0.4 mm. Hg over a period of about 1 hour and 10 minutes. The so obtained modified polyester had an intrinsic viscosity of 0.45 and a softening point of 252.3° C.

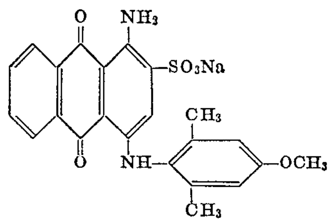
Fifty parts of this modified polyester which had been prepared into particle sizes having maximum diameters of 3–5 mm. and 19 parts of polycaproamide having an intrinsic viscosity of 0.64 and softening point of 213.7° C. and similarly prepared into particle sizes having maximum diameters of 3–5 mm. were mixed and charged to an autoclave which, after being purged with nitrogen, was reduced to a pressure of less than 2 mm. of Hg. After the temperature was brought to 275° C. and the two polymers were thoroughly melted by being held at this temperature for 30 minutes, the stirring of the blend was carried out for 30 minutes. The resulting blend had a softening point of 249.9° C.

After vacuum drying this polymer at 100° C. for 4 hours, it was spun at 275° C. and a spinning speed of 700 meters per minute. The resulting fiber, after being drawn 4.3×, had a denier fineness of 3.2, a tensile strength of 4.2 g./den. and an elongation at break of

38%. This fiber was dipped in a dye bath of the following composition.

Acid dye (C.I. Acid Blue 129) [a]	percent (O.W.F.)	4
n-Tetrabutylammonium chloride	do	10
Actinol R–100, a nonionic surfactant primary polyoxyethylene lauryl ether	g./liter	1
Bath ratio		1:50

[a] Formula:



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 2

An autoclave was charged with 291 parts of dimethyl terephthalate, 207 parts of ethylene glycol, 30 parts of methoxypolyoxyethylene glycol (molecular weight about 1000), 0.816 part of pentaerythritol, 0.102 part of calcium acetate monohydrate and 0.75 part of antimony trioxide, after which the autoclave was gradually heated while slowly introducing nitrogen thereinto. The temperature was raised to 225° C. over a period of about 3 hours while distilling off the methanol formed as a result of the ester-interchange reaction. After completion of the distillation off of the methanol, 0.051 part of phosphoric acid was added and the temperature was raised to 275° C. After stirring the reaction mixture at this temperature for about 30 minutes at atmospheric pressure, the pressure of the reaction system was slowly reduced to below 0.3 mm. Hg over a period of about 2 hours. The so obtained modified polyester had an intrinsic viscosity of 0.46 and a softening point of 254.4° C.

On the other hand, 101.8 parts of caprolactam and 169.8 parts of hexamethylenediammonium terephthalate, after being rendered into powder form, were thoroughly mixed and charged to an autoclave. After thorough purging of the atmosphere with nitrogen, the temperature of the autoclave was raised to 275° C. The autoclave was allowed to stand still in this state for 15 minutes while eliminating the distillate in the meanwhile. Next, agitation was carried out under atmospheric pressure for 2 hours and thereafter the pressure of the system was reduced to 4 mm. Hg in 15 minutes to eliminate the low-boiling components. The so obtained copolyamide had an intrinsic viscosity of 0.55 and a softening point of 251.0° C.

The modified polyester and copolyamide, obtained as described above, were then both rendered into granular form of maximum particle diameters 3–5 mm. Fifty parts of the modified polyester and 10 parts of the copolyamide were thoroughly mixed and charged to an autoclave. After purging with nitrogen, the pressure of the autoclave was reduced to below 3 mm. Hg and the temperature was raised to 275° C. After holding this temperature for 30 minutes to thoroughly melt the two polymers, stirring was carried out for 30 minutes. The so obtained blend had a softening point of 252.4° C.

After vacuum drying this polymer at 100° C. for 5 hours, it was spun at 275° C. at a spinning speed of 600 meters per minute. The denier fineness of the resulting fiber drawn 4.5× was 2.8, its tensile strength was 4 g./den. and its elongation at break was 46%.

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

	Percent (O.W.F.)
Acid dye (C.I. Acid Red 6, C.I. 14680)	4
n-Tributylamine	10
Univadine W, a nonionic surfactant	4
Sulfuric acid	3
Bath ratio, 1:50.	

When the dyeing was carried out at 120° C. for 90 minutes, it was possible to obtain a product dyed brightly to a deep shade of red.

EXAMPLE 3

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 thereinto. 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 so obtained modified polyester had an intrinsic viscosity of 0.50 and a softening point of 258.1° C.

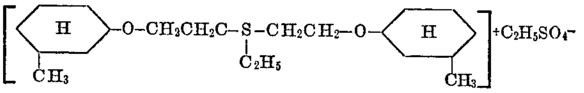
The modified polyester thus obtained and the copolyamide of the same sample as used in Example 2 were both rendered into granular form having maximum particle diameters from 3 mm. to 5 mm. or less. Fifty parts of this modified polyester and 5 parts of the copolyamide were thoroughly mixed and charged 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.

	Percent (O.W.F.)
Acid dye (C.I. Acid Blue 129)	4
([a])	10
Univadine W	3
Bath ratio, 1:50.	

[a] Formula:



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

EXAMPLE 4

(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 at from 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 aforesaid 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.

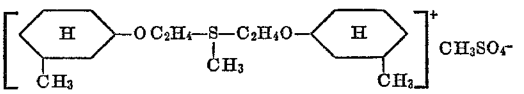
(d) Dyeing

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

	Percent (O.W.F.)
Acid dye (C.I. Acid Blue 129)	4
n-Tributyllaurylammonium bromide	10
Actinol R–100, 1 g./liter	
Bath ratio, 1:50	

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

Instead of n-tributyllaurylammonium chloride in the foregoing dye bath, the following compounds were also used.

(1) Tributylamine,
(2) Lauryldimethyl 2-chlorobenzylammonium chloride,
(3)


and
(4) Triamylamine.

It was possible to obtain products brightly dyed to deep shades of the blue of Grade 9 in these cases also.

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, C.I. 11110) 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 made during the dyeing. The polyester fiber obtained by the method of Example 4–(a)(b)(c) was dipped in a dye bath of the following composition.

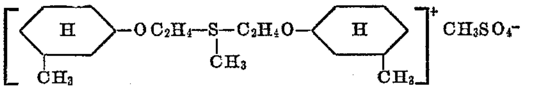
	Percent (O.W.F.)
Acid dye (C.I. Acid Blue 129)	4
Acetic acid	3
Actinol R–100, 1 g./liter	

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

EXAMPLE 5

Twenty parts of a copolyamide ($\eta_{sp/c}$=0.54) consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium 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 4.3X 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 so obtained fiber was dyed using a dye bath composed of 4% (O.W.F.) of an acid dye Nylomin Blue GS (1. C.I.) (C.I. 62055), 5% (O.W.F.) of acetic acid, 4% (O.W.F.) of nonylphenoxypolyoxyethylene glycol and 4% (O.W.F.) of

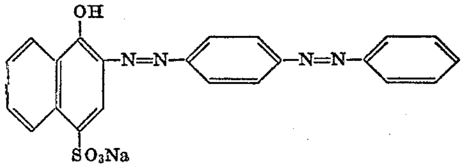


and under the conditions of a bath ratio 1:100 and 120° C. x 60 minutes, with the consequence that the fiber was dyed to a deep blue shade (Grades 8–9).

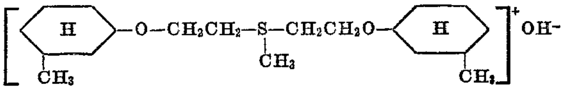
EXAMPLE 6

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 5, 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 ot 4% (O.W.F.) of Eriosin Red 2BX, A.C.I. Acid Red 116 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 (Grades 8–9).

EXAMPLE 7

Twenty parts of polymethoxylylene adipamide

($\eta_{sp/c}$=0.59)

was blended with 180 parts of 3 mol percent isophthalic component-copolymerized polyethylene terephthalate ($\eta_{sp/c}$=1.05), as in Example 5, after which the resulting blend was melt-spun at a spinning temperature of 280° C. in customary manner. The freshly spun filaments were then drawn 4.42× by means of an 85° C. pin, followed by being shrunk 22% at 205° C. and thereafter again being drawn 10% at 160° C.

The so obtained fiber was dyed using a dye bath composed of 4% (O.W.F.) of an acid dye Nylomin Blue GS–4, 5% (O.W.F.) of acetic acid, 4% (O.W.F) of nonylphenoxypolyoxyethylene glycol and 10% (O.W.F.) of tetrabutylphosphonium bromide, and under the condition of a bath ratio 1:100 and 120° C. x 60 minutes. A dyed product of deep blue shade (Grades 8–9) was obtained.

EXAMPLE 8

Twenty parts of a copolyamide ($\eta_{sp/c}=0.54$) consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium terephthalate was melt-blended with 80 parts of polyethylene terephthalate ($\eta_{sp/c}=1.05$) at 285° C. for 10 minutes, after which the resulting blend was spun at a spinning speed of 285° C. in customary manner. The freshly spun filaments were drawn 4.3× 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. A dye bath composed of 4% (O.W.F.) of Nylomin Blue GS, 5% (O.W.F.) of acetic acid, 4% (O.W.F.) of nonylphenoxypolyoxyethylene glycol and 4% (O.W.F.) of triphenylbutylphosphonium chloride was used and the foregoing fiber was dyed under the conditions of a bath ratio 1:100 and 120° C. x 60 minutes, with the consequence that the fiber was dyed to a deep blue shade (Grades 8–9).

When the dyeing was carried out in a similar manner as described hereinabove but using instead of triphenylbutylphosphonium chloride the several compounds as indicated in the following table, the fiber was likewise dyed to deep shades of blue.

Compound:	Grade
Tri-n-butylamine	6
Triallylamine	5
n - Lauryldimethyl - 2 - nitrobenzylammonium bromide	7
n - Lauryldimethyl - 2 - chlorobenzylammonium chloride	8
n-Tetrabutylammonium chloride	8

On the other hand, when the dyeing was carried out using a dye bath composed of 4% (O.W.F.) of a basic dye Malachite Green, C.I. 42000 3% (O.W.F.) of acetic acid and 5% (O.W.F.) of sodium dodecylbenzenesulfonate and under the conditions of a bath ratio 1:100 and 120° C. x 90 minutes, a deep green shade (Grade 8) was obtained. Again, when a disperse dye of this fiber (Dispersol Fast Scarlet B, C.I. 11110) was used, the dye adsorption was 88.2%.

EXAMPLE 9

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 8, and the resulting blend was melt-spun at a spinning temperature of 285° C. in customary manner. The freshly spun filaments were drawn 4.25× by means of an 87° C. pin, then shrunk 30% at 215° C., and thereafter again drawn 15% at a temperature of 160° C.

When the so obtained fiber was dyed with the acid dye Nylomin Blue GS as in Example 8, it was dyed to a deep blue shade (Grade 8). On the other hand, it was dyed to a deep green shade (Grades 7–8) by means of the basic dye Malachite Green.

EXAMPLE 10

Twenty parts of polymetaxylene adipamide ($\eta_{sp/c}=0.59$) was melt-blended with 180 parts of 3 mol percent isophthalate component-copolymerized polyethylene terephthalate ($\eta_{sp/c}=1.05$), as in Example 8, after which the resulting blend was melt-spun at a spinning temperature of 280° C. in customary manner. The freshly spun filaments were drawn 4.42× by means of an 85° C. pin, then shrunk 22% at 205° C., and thereafter again drawn 10% at 160° C.

When the so obtained fiber was dyed as in Example 8 with the acid dye Nylomin Blue GS, it was dyed to a deep blue shade (Grades 8–9). On the other hand, when it was dyed with the basic dye Malachite Green, it was dyed to a deep green shade.

EXAMPLE 11

In preparing a copolyamide consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium terephthalate, polyoxyethylene glycol (molecular weight about 4000) was blended therewith in such an amount that the content of the latter in the copolyamide would become 20% by weight. Forty parts of the so obtained blend and 160 parts of polyethylene terephthalate ($\eta_{sp/c}=1.05$) were then blended as in Example 8 ($\eta_{sp/c}$ of the blend=0.45). This blend was spun in customary manner at a spinning temperature of 285° C. The freshly spun filaments were then drawn 4.14× by means of an 85° C. pin, then shrunk 20% at 200° C. and thereafter again drawn 17% at 140° C. When this fiber was dyed as in Example 8, it was dyed to a deep blue shade (Grade 9) by means of the acid dye Nylomin Blue GS and was dyed to a deep green shade (Grade 9) by means of the basic dye Malachite Green.

EXAMPLE 12

Twenty parts of a copolyamide ($\eta_{sp/c}=0.488$) consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium terephthalate and 0.05 mol percent pentaerythritol-copolymerized polyethylene terephthalate ($\eta_{sp/c}=0.979$) were melt-blended at 285° C. for 20 minutes, following which the resulting blend was spun in customary manner at a spinning speed of 285° C. The freshly spun filaments were drawn 3.9× by means of a 90° C. pin, then shrunk 27% at 235° C., and thereafter again drawn 12% at 160° C. The so obtained fiber was dyed as in Example 8. It was dyed to a deep blue shade (Grade 8) by means of acid dye Nylomin Blue GS and to a deep green shade (Grade 7) by means of the basic dye Malachite Green.

EXAMPLE 13

Twenty parts of a copolyamide consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium terephthalate was melt-blended with 80 parts of polyethylene terephthalate and then spun in customary manner at a spinning temperature of 285° C. The freshly spun filaments were drawn 4.3× by means of an 85° C. pin followed by again drawing with a pin heated at 80° C.

The so obtained fiber was dyed using a dye bath composed of 4% (O.W.F.) of the acid dye Nylomin Blue GS, 5% (O.W.F.) of acetic acid, 4% (O.W.F.) of nonylphenoxypolyoxyethylene glycol and 4% (O.W.F.) of butylstearylammonium chloride, and under the conditions of a bath ratio 1:100 and 120° C. x 60 minutes. A product dyed to a deep blue shade (Grades 5–6) was obtained.

EXAMPLE 14

Twenty parts of polymetaxylene adipamide was blended with 180 parts of 3 mol percent isophthalic acid component-copolymerized polyethylene terephthalate, after which the resulting blend was melt-spun in customary manner at a spinning temperature of 280° C. The freshly spun filaments were drawn 4.2× by means of a pin heated at 80° C.

When the so obtained fiber was dyed as in Example 13, it was dyed to a deep blue shade (Grade 5–6) by means of the acid dye Nylomin Blue GS.

EXAMPLE 15

An acetate cloth was dyed for 60 minutes at 80° C. in a dye bath of the following composition:

	Percent (O.W.F.)
C.I. Acid Red 6, C.I. 14680	3
Tributylbenzylammonium chloride	3
2,2′-4,4′-tetrahydroxybenzophenone	5
Sodium carbonate	10
Bath ratio, 1:50	

After completion of the dyeing, soaping of the cloth was carried out for 30 minutes at 60° C. in a 0.2% solution of Scourol 400 (a trade name of a nonionic surfactant). The result was a dyed product of a bright red shade. This dyed product was exposed to light for 20 hours in a Fade-O-meter, but no fading whatsoever was observed. When, as control, a specimen dyed in a dye bath of the above composition but which did not contain 2,2'-4,4'-tetrahydroxybenzophenone was exposed similarly for 20 hours in the Fade-O-meter, the fading was marked.

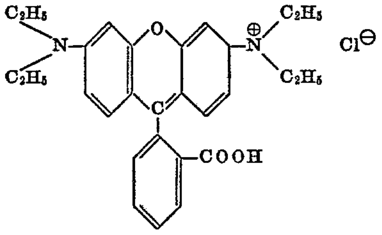
EXAMPLE 16

A "Valren" (a polyvinyl chloride fiber) cloth was dyed at 80° C. for 60 minutes in a dye bath of the following composition:

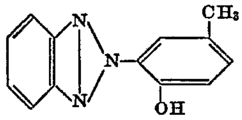
	Percent (O.W.F.)
Basolan Brilliant Red FFB [a]	4
Tributylamine	4
Tinuvin P [b]	2
Acetic acid	4

Bath ratio, 1:50

[a] C.I. Basic Violet 10 of the formula:



[b] Formula:



Soaping was carried out under identical conditions as in Example 15, with the consequence that a cloth dyed to a bright shade of pink was obtained. When this product was exposed for 40 hours in a Fade-O-meter, little, if any, fading was observed.

On the other hand, when, as control, a specimen dyed in a dye bath of the above composition but from which Tinuvin P was eliminated was similarly exposed for 40 hours in the Fade-O-meter, the fading of the cloth was marked.

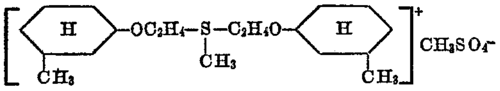
EXAMPLE 17

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

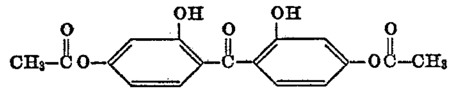
	Percent (O.W.F.)
Xylene Fast Blue PR [a]	1
2,2'-dihydroxy - 4,4'-diacetylbenzophenone [b]	2
Acetic acid	2
P.P.C. [c]	20

Bath ratio, 1:100

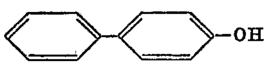
[a] Formula:



[b] Formula:



[c] Formula:



When soaping was carried out as in Example 15 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 control, a specimen dyed in a dye bath of the above composition but from which was eliminated the 2,2'-hydroxy-4,4'-diacetylbenzophenone was similarly exposed for 40 hours in a Fade-O-meter, marked fading occurred.

EXAMPLE 18

An autoclave was charged with 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 and gradually heated while slowly introducing nitrogen thereinto. The temperature was raised to 230° C. over a period of about 3½ hours while distilling off the methanol formed as a result of the ester-interchange reaction. After completion of the distillation off of the methanol, 0.051 part of phosphoric acid was added and the temperature was raised to 275° C. Stirring was carried out at this temperature for 30 minutes under atmospheric pressure, following which the pressure of the reaction system was reduced to below 0.4 mm. Hg over a period of about one hour and 10 minutes. The intrinsic viscosity of the so obtained polyester was 0.45 and its softening point was 252.3° C.

Fifty parts of this polyester which had been rendered into granular form having maximum particle diameters of 3–5 mm. and 19 parts of polycaproamide having an intrinsic viscosity of 0.64 and a softening point of 213.7° C. which had likewise been rendered into granular form having maximum particle diameters of 3–5 mm. were mixed and charged to an autoclave. The pressure of the autoclave, after purging with nitrogen, was reduced to below 2 mm. Hg. The temperature was raised to 275° C. where it was held for 30 minutes to accomplish the thorough melting of the two polymers, after which stirring was carried out for 30 minutes to obtain a blend having a softening point of 249.9° C. After this polymer was vacuum dried at 100° C. for 4 hours, it was spun at 275° C. and a spinning speed of 700 meters per minute.

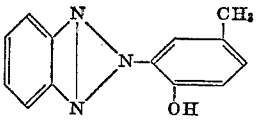
The freshly spun filaments drawn 4.3× at 70° C. had a denier fineness of 3.2, a tensile strength of 4.2 g./den. and an elongation breakage of 38%.

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

	Percent (O.W.F.)
Xylene Fast Blue PR	1
Tributylbenzylammonium chloride	1
Acetic acid	3
Tinuvin P [a]	2

Bath ratio, 1:50

[a] Formula:



After dyeing at 120° C. for 90 minutes, soaping of the fiber was carried out for 30 minutes at 80° C. in a 0.2% solution of Marseilles soap. As a result, a product dyed to a blue shade was obtained.

This dyed product was exposed for 80 hours in a Fade-O-meter, but no fading could be observed in the least.

As control, the fiber was dyed in a bath of the above composition except that the Tinuvine P was eliminated. Although a product dyed to a blue shade was similarly obtained as in the case described previously, the fading in this case was marked when exposed for 80 hours in the Fade-O-meter.

EXAMPLE 19

(a) Preparation of a blend of a polyamide and a polyoxyalkylene glycol

250 parts of hexamethylenediammonium adipate and 56 parts of methoxypolyoxyethylene glycol were dissolved in 300 parts of water and charged to a polymerization vessel. After purging with nitrogen, the vessel was slowly heated and the water distilling off was eliminated. The

temperature of the residuum was raised to 280° C., at which temperature stirring was carried out for 60 minutes, after which the pressure of the system was gradually reduced to 0.7 mm. Hg at which the polymerization reaction was carried out for 20 minutes. The $\eta_{sp/c}$ of the resulting polyamidepolyoxyalkylene glycol blend was 1.13.

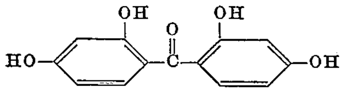
(b) Preparation of the polyester composition

Thirty-five parts of the foregoing blend and 165 parts of the polyester obtained in Example 18 were blended as described in said example, following which the so obtained blend was spun and the resulting filaments were drawn as described therein. The so obtained fiber was dipped in a dye bath of the following composition.

	Percent (O.W.F.)
Suminol Fast Red B	3
Tributylamine	3
2,2',4,4'-tetrahydroxybenzophenone [a]	5
Acetic acid	5

Bath ratio, 1:50

[a] Formula:



After the fiber was dyed for 60 minutes at 120° C. in the foregoing dye bath, it was soaped for 30 minutes at 80° C. in a 0.2% solution of Marseilles soap. The result was a product dyed to a bright shade of red. Although this dyed product was exposed for 80 hours in a Fade-O-meter, no fading was noted at all. When, as control, a specimen dyed in a dye bath of the foregoing composition but from which the 2,2',4,4'-tetrahydroxybenzophenone was eliminated was similarly exposed for 80 hours in the Fade-O-meter, marked fading was noted.

EXAMPLE 20

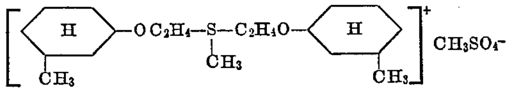
Twenty parts of a copolyamide ($\eta_{sp/c}=0.54$) consisting of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium terephthalate was melt-blended with 80 parts of polyethylene terephthalate ($\eta_{sp/c}=0.63$) for 10 minutes at 285° C. under nitrogen, after which the resulting blend was spun in customary manner at a spinning temperature of 285° C. The freshly spun filaments were drawn 4.3× 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 so obtained fiber was dipped in a dye bath of the following composition:

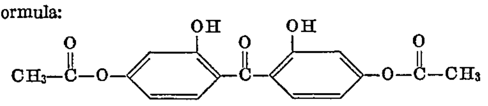
	Percent (O.W.F.)
Xylene Brilliant Blue 5 GM (C.I. Acid Blue 142)	4
(a)	4
2,2-dihydroxy-4,4'-diacetylbenzophenone [b]	4
Acetic acid	3

Bath ratio, 1:50

[a] Formula:



[b] Formula:



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 as in Example 18. 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-O-meter, there was observed no fading at all. When, as control, a specimen dyed in a dye bath of the above composition but from which 2,2'-dihydroxy-4,4'-diacetylbenzophenone was eliminated was similarly exposed for 40 hours in a Fade-O-meter, marked fading was noted.

EXAMPLE 21

A polyvinyl chloride fiber "Valren" was dipped in a dye bath of the following composition and dyed at 100° C. for 60 minutes, whereupon a product dyed to a deep shade of blue was obtained.

	Percent (O.W.F.)
C. I. Acid Blue 129	3
n-Triamylamine	10
Univadine W	3
Acetic acid	3

Bath ratio, 1:50

EXAMPLE 22

A polyvinyl chloride fiber "Teviron" (trademark of Teijin Limited) was dipped in a dye bath of the following composition:

	Percent (O.W.F.)
Suminol Fast Red B conc.	3
n-Triamylamine	10
Methyl naphthalene (carrier)	6
Univadine W	3
Sulfuric acid	3

Bath ratio, 1:50

As a result of dyeing at 50° C. for 90 minutes, a product dyed to a deep shade of red was obtained.

EXAMPLE 23

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

	Percent (O.W.F.)
Kayanol Milling Yellow 3 GW (C.I. Acid Yellow 72)	3
n-Tributylamine	5
Methyl naphthalene (carrier)	3
Acetic acid	3

Bath ratio, 1:50

When the fiber was dyed at 100° C. for 60 minutes in the foregoing dye bath, a product dyed to a deep shade of yellow was obtained.

EXAMPLE 24

A polyacrylonitrile fiber was dipped in a dye bath of the same composition as that described in Example 21. After dyeing at 100° C. for 60 minutes, a product dyed to a deep shade of blue was obtained.

EXAMPLE 25

An acrylonitrile fiber "Orlon" was dipped in a dye bath of identical composition as that of Example 23 and dyed at 120° C. for 90 minutes, whereupon a product dyed to a deep shade of yellow was obtained.

EXAMPLE 26

As a cellulose acetate textile, a crepe de chine fabric of diacetate fiber was used. This was dipped in a dye bath of the following composition:

	Percent (O.W.F.)
Kayacyl Sky Blue R (C.I. 62045)	4
Triamylamine	10
Univadine W	4
Sulfuric acid	3

Bath ratio, 1:50

When the fabric was dyed at 100° C. for 90 minutes, a product dyed to a deep shade of blue was obtained. Again, when tributylamine was used instead of triamylamine and the dyeing was carried out in like manner, a product dyed likewise to a deep shade of blue was obtained.

EXAMPLE 27

The polyester fiber, "Tetoron" T-89 was dipped in a dye bath of the same composition as that of Example 26 and dyed at 120° C. for 90 minutes, with the result that a product dyed to a deep shade of blue was obtained,

EXAMPLE 28

As a modified polyester fiber, "Torevira WA" (dye adsorption 85%) was used. This was dipped in a dye bath of the following composition:

	Percent (O.W.F.)
Polar Yellow 5 GN	4
N,N-diamylaniline	10
Univadine W	4
Orthophenylphenol	4
Acetic acid	2

When the fiber was dyed at 120° C. for 90 minutes in the foregoing bath, a product dyed to a deep shade of yellow was obtained.

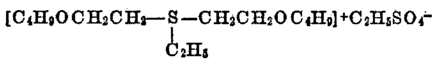
EXAMPLE 29

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

	Percent (O.W.F.)
Xylene Fast Blue PR [a]	2
Univadine W	2

Bath ratio, 1:50

[a] Formula:



$$[C_4H_9OCH_2CH_2-\underset{\underset{C_2H_5}{|}}{S}-CH_2CH_2OC_4H_9]^+C_2H_5SO_4^-$$

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%.

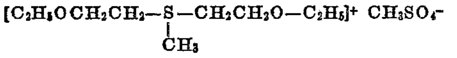
EXAMPLE 30

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

	Percent (O.W.F.)
Suminol Fast Red B (C.I. Acid Red 6	3
(a)	3
Univadine W	2

Bath ratio, 1:50

[a] Formula:



$$[C_2H_5OCH_2CH_2-\underset{\underset{CH_3}{|}}{S}-CH_2CH_2O-C_2H_5]^+\ CH_3SO_4^-$$

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%.

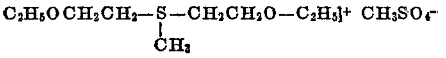
EXAMPLE 31

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

	Percent (O.W.F).
Suminol Fast Red B (C.I. Acid Red 6)	3
(a)	3

Trichlorobenzene (carrier), 3 g./liter
Univadine W, 2 g./liter.
Bath ratio, 1:50

[a] Formula:



$$C_2H_5OCH_2CH_2-\underset{\underset{CH_3}{|}}{S}-CH_2CH_2O-C_2H_5]^+\ CH_3SO_4^-$$

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

EXAMPLE 32

The dyeing was carried out at 60° C. for 60 minutes as in Example 30, except that the polyvinyl chloride fiber "Tevilon" was used instead of "Valren." A product dyed to a bright shade of red was obtained.

EXAMPLE 33

The dyeing was carried out at 100° C. for 60 minutes as in Example 29 except that a metal-containing dyestuff "Kayakalan Red 2BL" (C.I. Acid Red 318) was used instead of the dyestuff used in Example 29, with the result that a product dyed to a deep shade of red was obtained.

EXAMPLE 34

The dyeing was carried out at 90° C. for 60 minutes as in Example 31, except that instead of the dyestuff used therein a reactive dye Remasole Red B (C.I. Reactive Red 22) was used, with the result that a product dyed to a deep shade of red was obtained.

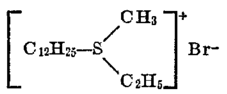
EXAMPLE 35

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

	Percent (O.W.F.)
Kayacyl Sky Blue R (C.I. Acid Blue 62)	5
(a)	10
Univadine W	5

Bath ratio, 1:50

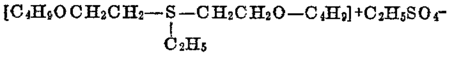
[a] Formula:



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 36

Example 35 was repeated except that instead of the cationic compound used therein



$$[C_4H_9OCH_2CH_2-\underset{\underset{C_2H_5}{|}}{S}-CH_2CH_2O-C_4H_9]^+C_2H_5SO_4^-$$

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

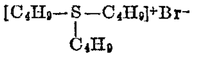
EXAMPLE 37

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

	Percent (O.W.F.)
Nylomin Yellow AGS (C.I. Acid Yellow 135)	4
(a)	10
Univadine W	4

Bath ratio, 1:50

[a] Formula:



$$[C_4H_9-\underset{\underset{C_4H_9}{|}}{S}-C_4H_9]^+Br^-$$

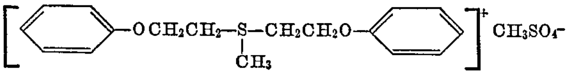
The dyeing was carried out at 80° C. for 120 minutes. After completion of the dyeing of the fabric, it was washed in a bath containing an anionic surfactant, whereupon a product brightly dyed to a deep shade of yellow was obtained.

EXAMPLE 38

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

	Percent (O.W.F.)
Kayacyl Sky Blue R	4
(a)	10
Univadine W	4
Soda ash, 1 g./liter	
Bath ratio, 1:50	

[a] Formula:



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.

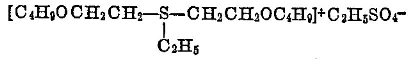
EXAMPLE 39

When the triacetate fiber was used instead of the diacetate fiber in Example 35 and the dyeing was carried out at 120° C. for 90 minutes, a product dyed to a deep shade of blue was obtained.

EXAMPLE 40

	Percent
Kayacyl Sky Blue (C.I. Acid Blue 62)	2
Thiodiethylene glycol	2
(a)	4
Indalca ABV (12%) (a paste consisting predominantly of locust bean green)	70
Water	22
Total	100

[a] Formula:



$$[C_4H_9OCH_2CH_2-\underset{\displaystyle C_2H_5}{\underset{|}{S}}-CH_2CH_2OC_4H_9]^+C_2H_5SO_4^-$$

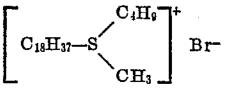
A crepe de chine fabric of diacetate fiber was printed using a paste of the foregoing composition. After drying the printed fabric, it was steamed at 100° C. for 40 minutes. The so-obtained dyed fabric was then waterwashed and laundered, whereupon was obtained a product which was dyed to a deep shade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

EXAMPLE 41

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

	Percent (O.W.F.)
Eriosin Red 2BX (C.I. Acid Red 116)	4
(a)	10
Univadine W	4
Bath ratio, 1:50	

[a] Formula:



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

EXAMPLE 42

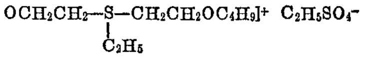
Example 41 was repeated except that the dyeing was carried out at 110° C. for 90 minutes using "Orlon" instead of the "Kanekalon" used therein. A product dyed to a deep shade of red was obtained.

EXAMPLE 43

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

	Percent (O.W.F.)
Lissamine Fast Violet 2BS (C.I. 62020) (C.I. Acid Violet 41)	4
(a)	10
Univadine W	4
Sulfuric acid, 1 g./liter	

[a] Formula:



$$OCH_2CH_2-\underset{\displaystyle C_2H_5}{\underset{|}{S}}-CH_2CH_2OC_4H_9]^+\ C_2H_5SO_4^-$$

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

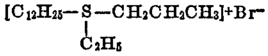
EXAMPLE 44

Example 43 was repeated except that Torevira WA (trademark of Hoechst Co.) was used as the modified polyester fiber instead of "Tetroron" T-89. A product dyed to a bright shade of purple was obtained.

EXAMPLE 45

	Percent
Eriosin Red 2 BX (C.I. Acid Red 116)	2
Liogen BC	5
([a])	10
Indalca ABV (12%)	60
Methyl naphthalene (carrier)	3
Water	20
Total	100

[a] Formula:



$$[C_{12}H_{25}-\underset{\displaystyle C_2H_5}{\underset{|}{S}}-CH_2CH_2CH_3]^+Br^-$$

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

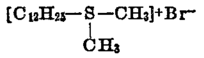
EXAMPLE 46

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-containing modified polyester fiber obtained as hereinabove described was dipped in a dye bath of the following composition:

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

[a] Formula:



$$[C_{12}H_{25}-\underset{\displaystyle CH_3}{\underset{|}{S}}-CH_3]^+Br^-$$

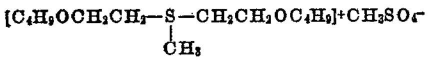
When the dyeing was carried out at 120° C. for 90 minutes, a product dyed brightly to a deep shade of blue was obtained.

EXAMPLE 47

The modified polyester fiber obtained in Example 46 was dipped in a dye bath of the following composition:

Eriosin Red 2 BX (C.I. Acid Red 116)	percent (O.W.F.)	4
(a)	do	10
Univadine W	do	4
Methyl naphthalene (carrier)	g./liter	3
Bath ratio		1:30

[a] Formula:



$$[C_4H_9OCH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{S}}-CH_2CH_2OC_4H_9]^+CH_3SO_4^-$$

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

EXAMPLE 48

The polyvinyl chloride fiber "Valren" (trademark of Teijin Limited) was dipped in a dye bath of the following composition where it was dyed at 100° C. for 60 minutes to obtain a dyed product of a deep blue shade.

	Percent (O.W.F.)
Suminol Fast Blue PR (C.I. Acid Blue 129)	3
Tributylbenzylphosphonium bromide	10
Univadine W	3
Acetic acid	3
Bath ratio, 1:50	

EXAMPLE 49

The polyvinyl chloride fiber "Tevilon" was dipped in a dyed bath of the following composition:

	Percent (O.W.F.)
Suminol Fast Red B conc.	3
Triphenylbutylphosphonium bromide	10
Methyl naphthalene (carrier)	6
Univadine W	3
Sulfuric acid	3
Bath ratio, 1:50	

When the dyeing was carried out at 50° C. for 90 minutes, a product dyed to a deep shade of red was obtained.

EXAMPLE 50

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

	Percent (O.W.F.)
Kayanol Milling Yellow 3 GW	3
Tributylbenzylphosphonium bromide	5
Methyl naphthalene (carrier)	3
Acetic acid	3
Bath ratio, 1:50	

When the dyeing was carried out at 100° C. for 60 minutes, a product dyed to a deep shade of yellow was obtained.

EXAMPLE 51

The polyacrylonitrile fiber "Kanekalon" was dipped in a dye bath of the same composition as that of Example 48. When the dyeing was carried out at 100° C. for 60 minutes, a product dyed to a deep shade of blue was obtained.

EXAMPLE 52

The polyacrylonitrile fiber "Orlon" was dipped in a dye bath of identical composition as that of Example 50. The dyeing was carried out at 120° C. for 90 minutes and a product dyed to a deep shade of yellow was obtained.

EXAMPLE 53

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

	Percent (O.W.F.)
Kayacyl Sky Blue R	4
Tributylbenzylphosphonium bromide	10
Univadine W	4
Sulfuric acid	3
Bath ratio, 1:50	

The dyeing was carried out at 100° C. for 90 minutes and a product dyed to a deep shade of blue was obtained.

EXAMPLE 54

The polyester fiber "Tetoron" T-89 was dipped in a dye bath of identical composition as that of Example 53, wherein it was dyed at 120° C. for 90 minutes to yield a product dyed to a deep shade of blue.

EXAMPLE 55

As a modified polyester fiber, "Tetoron" T-89 (dye adsorption of 85%) was used, and this fiber was dipped in a dye bath of the following composition:

	Percent (O.W.F.)
Polar Yellow 5 GN (C.I. Acid Yellow 110)	4
Triphenylethylphosphonium bromide	10
Univadine W	4
Orthophenylphenol	4
Acetic acid	2

When the fiber was dyed at 120° C. for 90 minutes, a product dyed to a deep shade (Grade 6) of yellow was obtained.

EXAMPLE 56

An autoclave was charged with 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. The autoclave was then gradually heated while slowly introducing nitrogen thereto, and the temperature was raised to 230° C. over a period of about 3½ hours while distilling off the methanol formed as a result of the ester-interchanging reaction.

After completion of the distillation off of the methanol, 0.051 part of phosphoric acid was added, following which the temperature was raised to 275° C. After stirring the reaction mixture at this temperature for 30 minutes under atmospheric pressure. the pressure of the reaction system was gradually reduced below 0.4 mm. Hg over a period of about one hour and 10 minutes.

The so obtained polyester had an intrinsic viscosity of 0.65 and a softening point of 252.4° C.

Fifty parts of the foregoing polyester and 10 parts of a polycaproamide having an intrinsic viscosity of 0.64 and a softening point of 213.7° C., both of which were rendered into particle size having maximum diameters 3-5 mm., were mixed and then charged to an autoclave which, after having been purged with nitrogen, was reduced to a pressure below 2 mm. Hg.

This was followed by raising the temperature of the autoclave to 275° C. where it was held for 30 minutes to effect the thorough melting of the two polymers, after which stirring was carried out for 30 minutes to obtain a blend having a softening point of 249.9° C. After vacuum drying this polymer at 100° C. for 4 hours, it was spun at 275° C. and a spinning speed of 700 meters per minute, after which the freshly spun filaments were drawn 4.3× to yield a fiber of 3.2 denier and having a tensile strength of 4.2 g./den. and an elongation at break of 38%.

The so obtained fiber was dipped in a dye bath of the following composition:

	Percent (O.W.F.)
Xylene Fast Blue PR	4
Triphenylphosphine	10
Acetic acid	[a] 4
Univadine W	4

Bath ratio, 1:50

[a] pH 3.

The fiber was dyed at 120° C. for 9 minutes and thereafter soaped at 80° C. for 30 minutes in a 0.2% solution of Marseilles soap, with the result that a product dyed to a blue shade was obtained.

Although the so obtained dyed product was exposed for 80 hours in a Fade-Ometer, no fading at all was observed.

EXAMPLE 57

(a) Preparation of a blend of a polyamide and a polyoxyalkylene glycol

250 parts of hexamethylenediammonium adipate and 56 parts of methoxypolyoxyethylene glycol (average molecular weight about 4000) were dissolved in 300 parts of water and charged to a polymerization vessel. After purging the nitrogen, the vessel was slowly heated and the water distilling off was eliminated.

The temperature of the residuum was then raised to 280° C., at which temperature stirring was carried out for 60 minutes, after which the pressure of the system was gradually reduced to 0.7 mm. Hg, at which the polymerization reaction was carried out for 20 minutes. The so obtained polyamide-polyoxyalkylene glycol blend had an $\eta_{sp/c}$ of 1.13.

(b) Preparation of the polyester compositon

Thirty-five parts of the foregoing blend and 165 parts of the polyester obtained in Example 56 were blended and spun, after which the resulting filaments were drawn, as described therein. The so obtained fiber was dipped in a dye bath of the following composition:

	Percent (O.W.F.)
Suminol Fast Red B	3
Tributylphosphine	5
Univadine W	3
Acetic acid	5

Bath ratio, 1:50

After the dyeing was carried out at 120° C. for 60 minutes, soaping of the fiber was carried out at 80° C. for 30 minutes in a 0.2% solution of Marseilles soap, with the result that a product dyed to a bright shade of red was obtained.

EXAMPLE 58

Twenty parts of a copolyamide ($\eta_{sp/c}=0.54$) composed of 70 mol percent of caprolactam and 30 mol percent of hexamethylenediammonium terephthalate and 80 parts of polyethylene terephthalate were spun in customary manner at 285° C. under nitrogen. The freshly spun filaments were drawn 4.3× 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 so obtained fiber was dipped in a dye bath of the following composition:

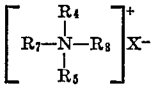
	Percent (O.W.F.)
Eriosin Red 2 BX (C.I. Acid Red 116)	4
Tributylphosphine	10

Bath adjusted to pH=2 with sulfuric acid
Bath ratio, 1:50

After carrying out the dyeing at 120° C. for 90 minutes, soaping was carried out as in Example 56, whereupon a product dyed to a bright shade of red was obtained. Although this dyed product was exposed in a Fade-O-meter for 40 hours, there was observed no fading at all.

We claim:

1. A method of dyeing a modified polyester textile fiber which comprises dyeing said fiber with an anionic dyestuff in the presence of a quaternary ammonium salt of the formula



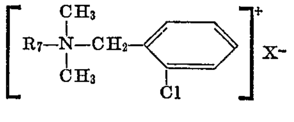
$$\left[R_7-\overset{\displaystyle R_4}{\underset{\displaystyle R_5}{N}}-R_8 \right]^+ X^-$$

wherein R_4 and R_5 are each selected from the group consisting of alkyl and alkenyl groups of 1–5 carbon atoms, R_7 is selected from the group consisting of alkyl and alkenyl groups of 5–18 carbon atoms, R_8 is selected from the group consisting of phenyl, benzyl, chlorobenzyl, naphthyl, alpha - naphthylmethyl, diphenyl and cycloalkyl groups, and X is selected from the group consisting of halogens, alkoxy sulfate and OH group.

2. The method according to claim 1 wherein said modified polyester fiber is one selected from the group consisting of:

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

3. The method to claim 2 wherein said compound is a quaternary ammonium salt of the formula



wherein R_7 is selected from the group consisting of alkyl and alkenyl groups of 5–18 carbon atoms and their derivatives, and X is selected from the group consisting of halogens, alkoxy sulfate and OH group.

References Cited

UNITED STATES PATENTS

2,989,360	6/1961	Mautner	8—172 X
2,893,815	7/1959	Stanley et al.	8—85 X
3,097,047	7/1963	Weinstein et al.	8—162 A
3,387,916	6/1968	Clarke	8—172 X
2,192,956	3/1940	Sloan et al.	106—308 N

OTHER REFERENCES

Exparte Schoonover et al., decision of the Board of Appeals, Pat. No. 2,743,991, Paper No. 23, 6 pages.

Exparte Schoeneberg et al., decision of the Board of Appeals, Pat. No. 3,190,718, Paper No. 27, 4 pages.

GEORGE F. LESMES, Primary Examiner

T. J. HERBERT, Jr., Assistant Examiner

U.S. Cl. X.R.

8—173, 169, 165, 175, 171; 260—45.8 N, 45.95, 45.85, 45.9 R