United States Patent Office 3,527,557 Patented Sept. 8, 1970

3,527,557

BASIC DYE ACCEPTANCE OF ACRYLONITRILE-POLYMER CONTAINING FIBERS

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No Drawing. Filed Dec. 27, 1966, Ser. No. 604,560
Int. Cl. D06m 11/00; D06p 5/04
U.S. Cl. 8—100 4 Claims

ABSTRACT OF THE DISCLOSURE

Basic dye acceptance of acrylonitrile-polymer containing fibers is improved by contacting the fiber with and reacting thereon an aqueous solution comprised of a phosphate ester and a substituted carbamyl compound. The reaction product formed on the fiber is water-insoluble and improves the basic dyeing of acrylic fibers.

BACKGROUND OF THE INVENTION

This invention relates to a process of improving the basic dye acceptance of acrylonitrile-polymer containing fibers and to the fibers treated by the process. More particularly the invention relates to a novel, water-insoluble finish on the fiber which improves the basic dye acceptance of acrylonitrile-polymer containing fibers, the finish comprised of the reaction product of a phosphate ester and a substituted carbamyl compound, and to fibers having thereon this finish.

Fibers composed of polymerized acrylonitrile are generally resistive to basic dyes. Basic dyes are desirable in coloring acrylonitrile-polymer containing fibers because of the brightness of shade imparted by these dyes, their brightness being unmatched by other types of dyes. To overcome this resistance to basic dyes, acrylonitrile has been copolymerized with vinyl carboxylates, e.g. vinyl acetate, and the resulting polymer spun into a fiber to give a fiber which has improved basic dyeability. However, such fibers are still difficult to dye with basic dyes to give dark or very dark colors.

One method of increasing the basic dye acceptance of acrylonitrile-polymer containing fibers is to treat the fiber with a swelling agent. Such a treatment swells or opens the fiber to allow dye molecules to penetrate the fiber to a greater number of dye sites. The swelling treatment however causes the fiber structure to change from a dense to a porous state resulting in an adverse affect on fiber strength and abrasion resistance.

Acid compounds have been incorporated into the fiber to impart greater affinity for basic dyes. This technique has generally resulted in a corrosive fiber which causes corrosion of textile processing equipment and such acid compounds are generally water-insoluble and thus are easily removed from the fiber by a water wash.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a process of improving the basic dye acceptance of acrylonitrile-polymer containing fibers.

Another object of this invention is to provide fibers having an improved basic dye acceptance.

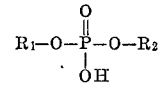
Still further, an object of this invention is to provide a process of imparting a water-insoluble finish on an acrylonitrile-polymer containing fiber which exhibits improved basic dye acceptance.

Other objects of this invention will become apparent as the invention is fully developed within the specification.

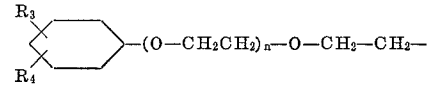
These and other objects of this invention are accomplished by providing a process of improving the basic dye acceptance of an acrylonitrile-copolymer containing fiber comprising contacting the fiber with and reacting thereon a water-soluble phosphate ester and a water-soluble carbamyl compound, to give a water-insoluble finish on the fiber.

DESCRIPTION OF THE INVENTION

The phosphate esters useful in this invention are water soluble and are a mixture of mono- and di- acid phophate esters defined by the formula:



wherein R_1 is selected from the group consisting of hydrogen and R_2, and R_2 is selected from the group consisting of an alkyl containing at least about 10 carbon atoms, and alkyl poly(oxyethylene) grouping wherein the alkyl contains at least 5 carbon atoms, and an alkyl phenol poly(oxyethylene) grouping. Preferably R_2 is an alkyl phenyl poly(oxyethylene) glycol residue defined by the formula:



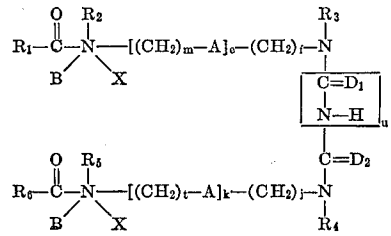
wherein R_3 is an alkyl grouping containing from about 5 to about 15 carbon atoms, R_4 is selected from the group consisting of hydrogen and an alkyl grouping containing from about 5 to about 15 carbon atoms and n is a whole integer from about 2 to about 30. More preferably, R_4 is in a position ortho to the repeating oxyethylene grouping. These phosphate esters may be obtained by reacting P_2O_5 with an appropriate hydroxyl compound to yield the desired phosphate ester. For example, one mole of P_2O_5 may be reacted with from about 2 to about 4.5 moles of an alkyl phenyl poly(oxyethylene) glycol under substantially anhydrous conditions and at about 212° F. to yield a useful phosphate ester. Examples of useful hydroxy compounds which may be reacted with P_2O_5 to produce useful phosphate esters with this invention are:

pentylphenylpoly(oxyethylene) glycol
di-(neopentyl)phenylpoly(oxyethylene) glycol
hexylphenylpoly(oxyethylene) glycol
2-ethylhexylphenylpoly(oxyethylene) glycol
di-(2-ethylhexyl)phenylpoly(oxethylene) glycol
octylphenylpoly(oxyethylene) glycol
nonylphenylpoly(oxyethylene) glycol
dodecylphenylpoly(oxyethylene) glycol
hexylpoly(oxyethylene) glycol
decylpoly(oxyethylene) glycol
dodecylpoly(oxyethylene) glycol
hexyldecylpoly(oxyethylene) glycol
octadecylpoly(oxyethylene) glycol
lauryl alcohol
2-ethylhexanol
capryl alcohol
octadecanol

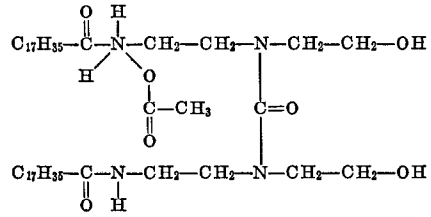
Other useful phosphate esters can be found in U.S. Pats. Nos. 3,004,056 and 3,004,057.

The mono- and di- acid phosphate esters described above normally have a pH within the range of from about 1.5 to about 3.5. When the acrylonitrile-polymer containing fiber has a relatively low pH, the addition of such phosphate esters may be sufficient to cause the fibers to become more corrosive to the textile processing equipment and thus be undesirable. In such a case, the phosphate esters can be neutralized with a weak base to a desired pH which is non-corrosive. For example, the phosphate esters can be neutralized with ammonium pentaborate to give a desired pH to the phosphate ester.

The substituted carbamyl compounds useful in this invention are water soluble and are defined by the formula:



wherein R_1 and R_6 are selected from the group consisting of an alkyl containing about 6 or more carbon atoms and an acyl radical containing about 6 or more carbon atoms; R_2, R_3, R_4 and R_5 are selected from the group consisting of hydrogen, an alkyl containing up to about 5 carbon atoms and a hydroxy substituted alkyl containing up to about 5 carbon atoms; D_1 and D_2 are selected from the group consisting of oxygen, sulphur, and imide; *u* is a whole integer from 0 to about 3; A is selected from the group consisting of amino radicals, an alkyl containing up to about 5 carbon atoms, a hydroxy substituted alkyl amino radical containing up to about 5 carbon atoms, oxygen and sulphur; *f*, *j*, *m* and *t* are whole integers from 1 to about 6; and *e* and *k* are whole integers from 0 to about 6; B is hydrogen or an alkyl group and X is an acid radical or halogen group. A preferred substituted carbamyl compound is defined by the formula:



Preparation of this compound is disclosed in U.S. Pat. No. 2,304,113 and is identified on the open market as Ahcovel A. Useful substituted carbamyl compounds can be obtained as a reaction product of the condensation of substituted ureas, substituted thioureas, substituted biurets, substituted guanidines, substituted biguanidines, and substituted guanyureas of high molecular weight.

As mentioned previously, the basic dye acceptance of acrylonitrile-polymer containing fibers can be improved by contacting the fiber with and reacting thereon a water soluble phosphate ester and a water soluble carbamyl compound. Contacting the fiber with the phosphate ester and the carbamyl compound can be effected by immersing the fiber in an aqueous finish bath comprised of the phosphate ester and the carbamyl compound. Also, the fiber can be contacted by spraying such an aqueous finish onto the fiber. The aqueous finish bath can contain from about 0.2 to about 2 percent of the substituted carbamyl compound and from about 1.0 to about 5 percent of the phosphate ester. The finish bath can contain other finishing agents, e.g. a lubricating agent, an antistatic agent and other types of agents to give desired properties to the fiber.

The water soluble phosphate ester and the water soluble substituted carbamyl compound react to form a water-insoluble finish on the fiber. Reaction is effected by heating the two compounds to a temperature above about 230° F. For example, the finish of this invention can be applied to undried, uncollapsed fiber by contacting the fiber with an aqueous bath containing from about 0.2 to about 2 percent of the substituted carbamyl compound and from about 1.0 to about 5 percent of the phosphate ester compound and then heating the fiber to a temperature of about 280° F. to dry the fiber and to react in situ on the fiber the carbamyl compound and the phosphate ester compound to form a water-insoluble finish thereon which exhibits improved basic dye acceptance.

Such a finish can also be applied with good results to fibers which have been collapsed to a dense structure by predrying the fiber and then applying the finish thereon, however, it is preferred that the finish be applied to undried and uncollapsed fiber.

As a practical example of this invention, basic dye acceptance can be imparted to acrylonitrile-polymer containing fibers by: wet spinning an appropriate dope through a conventional spinnerette into an aqueous coagulation bath wherein the extruded dope hardens into a filamentary fiber, then washing the fibers to remove residual solvent in the extruded dope, drawing the fibers to achieve molecular orientation, then contacting the fibers with an aqueous finish solution comprised of the phosphate ester and the substituted carbamyl compound and then passing the fibers over a series of heated rolls to react the phosphate ester and the carbamyl compound in situ on the fiber and to dry the fiber. Contacting the fibers can be accomplished by immersing the fibers in such a finish solution or the finish can be sprayed onto the fibers. After the fibers are contacted with the aqueous finish solution, they are passed over a series of heated rolls to dry and react the phosphate ester with the carbamyl compound. The drying and the reaction can also be accomplished by passing the fibers through an oven heated at a temperature of about 230° F. The dried fibers containing the reaction product of this invention can then be crimped and processed as tow or staple according to conventional textile processing techniques.

As previously mentioned, the aqueous finish solution can contain other agents in addition to the phosphate ester and the carbamyl compound. Such agents are sometimes desirable to enhance textile processing characteristics. Typically, it is desirable to include lubricating agents such as sorbitan monopalmitate, castor fatty acid, dispersing or emulsifying agents and other desirable agents useful in finish baths of conventional textile processing techniques.

The following examples are submitted to illustrate specific working embodiments of the invention. The samples within the examples are tested for basic dye acceptance, herein abbreviated as BDA, by measuring the amount of dye absorbed in each sample after it has been immersed for two hours in an aqueous dye bath at 206° F., the dyebath containing 20 percent of C. I. Name Basic Blue 22 (Sevron Blue 2G), 5 percent of ammonium acetate and 1 percent of acetic acid. The BDA is reported as percent dye on weight of fiber, and is determined by measuring the optical density of the exhausted dyebath on a Bausch and Lomb Model 505 Spectrophotometer and calculating the amount of dye remaining in the dyebath, then calculating the BDA as follows:

$$\text{Percent } BDA = \frac{\left(\begin{matrix}\text{wt. of dyestuff}\\ \text{added to bath}\end{matrix}\right) - \left(\begin{matrix}\text{wt. of dyestuff}\\ \text{remaining in bath}\end{matrix}\right)}{\text{weight of fiber dyed}} \times 100$$

The percent BDA is indicative of the affinity of the fiber for basic dyes. Unless otherwise specified, all percents are based on weight. The components used in the following examples are identified as:

Component in finish solution:	Description
Ahcovel A	Previous description.
Lubricant	60 percent sorbitan monopalmitate, 40 percent castor fatty acid reacted with ethylene oxide.
Antistat	Soya dimethylaminoethyl ethosulfate.
Ester #1	Reaction product of 1 mole P_2O_5 with 3.5 moles $C_9H_{19}C_6H_4(OC_2H_4)_{10}—OH$.
Ester #2	Reaction product of 1 mole P_2O_5 with 3.0 moles $(C_8H_{17})_2C_6H_3(OC_2H_4)_{12}OH$

Component in finish solution: Description

Ester #3 ---- Reaction product of 1 mole P_2O_5 with 3.0 moles $C_6H_{13}C_6H_4(OC_2H_4)_8$—OH.

Ester #4 ---- Reaction product of 1 mole P_2O_5 with 3.5 moles $C_6H_{13}(OC_2H_4)_{10}OH$.

Ester #5 ---- Reaction product of 1 mole P_2O_5 with 2.5 moles $C_{10}H_{21}(OC_2H_4)_8$—OH.

Ester #6 ---- Reaction product of 1 mole P_2O_5 with 3.5 moles of 2-ethyl hexanol.

Ester #7 ---- Reaction product of 1 mole P_2O_5 with 3.0 moles of lauryl alcohol.

Ester #8 ---- Reaction product of 1 mole P_2O_5 with 3.0 moles of octadecanol.

Example 1

A 3 denier acrylic sample (control sample) composed of 93 percent acrylonitrile and 7 percent vinyl acetate is drawn 4.5× after extrusion and is passed through an aqueous finish solution, herein identified as a Standard Solution throughout the examples, composed of (percents based on weight of finish):

	Percent
(1) Ahcovel A	0.3
(2) Antistat	0.9
(3) Lubricant	1.8

The fibers are dried over a series of hot rolls at 280° F., crimped, and collected. The fibers are then relaxed in a steam autoclave operated at 280° F., cut to a 2 inch staple length and are then carded. The carded sliver is then tested for BDA in accordance to the above described procedure. Additional samples (test samples) are treated as described above except the aqueous bath solution contains the below indicated components. Test results are indicated in Table I:

TABLE I

Sample	Aqueous finish solution	Basic dye acceptance percent	Percent increase over control sample
1---- Control---	Standard	5.6	
2---- Test----	Standard+1% Ester #1	6.6	18
3----do----	Standard+0.5% Ester #7	6.9	23
4----do----	Standard+1% Ester #7	7.2	28
5----do----	Standard+2% Ester #7	8.2	46
6----do----	0.5% Ahcovel A + 1% Ester #3.	7.5	34
7----do----	0.5% Ahcovel A + 1% Ester #4.	7.0	25

Example 2

Acrylic fiber samples described in Example No. 1 are treated as described in Example No. 1 except samples are contacted with an un-neutralized finish solution and a neutralized finish solution neutralized with ammonium pentaborate to a pH of 6. The BDA of these samples is determined as described above and the results are indicated in Table II:

TABLE II

Sample	Aqueous Finish Solution	Basic dye acceptance (percent) Neutralized Finish (pH=6)	Basic dye acceptance (percent) Un-neutralized Finish
1----	Standard+1% Ester #1	7.6	6.6
2----	Standard+0.5% Ester #7	8.3	6.9
3----	Standard+1% Ester #7	9.1	7.2

Example 3

Acrylic fiber samples described in Example 1 are treated as described in Example No. 1 except the aqueous finish solution is applied on the fiber after the fiber is partially dried to a moisture content of about 2.0 percent and half of the samples are treated with a neutralized finish solution. The predrying causes the fiber structure to collapse so that there is little penetration of the finish into the fiber.

After the aqueous finish solution is applied, the fiber is dried to a moisture content of below 1 percent and is processed as described in Example 1. The samples are analyzed for BDA and the results are compared with similar samples of Examples 1 and 2. Table III indicates the compositions of the aqueous finish solutions and the results of the BDA testing:

TABLE III

Sample	Aqueous Finish Solution	Basic dye acceptance (percent) Un-neutralized finish Std. Proc.	Un-neutralized finish Pre-dried	Neutralized finish Std. Proc.	Neutralized finish Pre-dried
1----	Standard	5.6	5.4		
2----	Standard +1% Ester #1	6.6	6.0	7.6	7.0
3----	Standard +0.5% Ester #7.	6.9	6.1	8.3	6.4
4----	Standard +1% Ester #7.	7.2	6.6	9.1	8.1

Example 4

Acrylic fiber samples having a denier of 3 and composed of a polymer being 90 percent acrylonitrile and 10 percent vinylidine chloride are treated as described in Example No. 1 except the aqueous finish solutions contain the below indicated compositions. The samples are analyzed for BDA and these results plus the composition of the aqueous finish solution are indicated in Table IV:

TABLE IV

Sample	Aqueous finish solution	BDA	Percent BDA increase over control sample
1---- Control---	1.5% Ahcovel A	1.1	
2---- Test----	0.5% Ahcovel A+1% Ester #6	1.6	45
3----do----	0.5% Ahcovel A+2% Ester #6	1.5	36
4----do----	0.5% Ahcovel A+4% Ester #6	2.2	100
5----do----	0.5% Ahcovel A+2% Ester #3	1.5	36

Example 5

Acrylic fiber samples described in Example No. 1 are treated as described in Example No. 1 except the aqueous finish solutions contain the below indicated components:

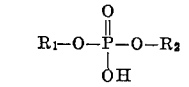
Sample 1: 1% Ahcovel A (Control)
Sample 2: 0.5% Ahcovel A+1% Ester #2
Sample 3: 0.5% Ahcovel A+1% Ester #5
Sample 4: 0.5% Ahcovel A+1% Ester #6

The BDA of the above samples is determined and the results of samples 2, 3 and 4 are found to be significantly greater than the BDA of sample 1.

This invention has been disclosed with respect to certain preferred embodiments, various modifications and variations thereof will become obvious to the person skilled in the art. It is to be understood that such modifications and variations are to be included within the spirit and purview of this application and the scope of the appended claims.

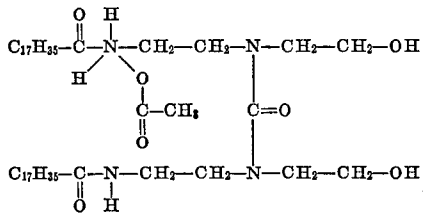
What is claimed is:

1. A process of improving the basic dye acceptance of an acrylonitrile-polymer containing fiber comprising contacting the fiber with an aqueous solution comprised of from about 1.0 to about 5 percent of a mixture of mono- and di- acid phosphate esters defined by the formula:



wherein R_1 is selected from the group consisting of hydrogen and R_2, and R_2 is selected from the group consisting of an alkyl containing at least about 10 carbon atoms, an alkyl poly(oxyethylene) grouping wherein the alkyl contains at least about 5 carbon atoms and an alkyl phenyl poly(oxyethylene) grouping; and from about 0.2

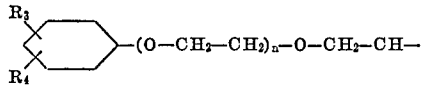
to about 2 percent of a substituted carbamyl compound defined by the formula:



and heating the fiber to a temperature of at least about 230° F.

2. The process of claim 1 wherein the fiber is heated to a temperature of about 280° F.

3. The process of claim 1 wherein R_2 of the phosphate ester is defined by the formula:



wherein R_3 is an alkyl containing from about 5 to about 15 carbon atoms, R_4 is selected from the group consisting of hydrogen and R_3, and n is a whole integer from about 2 to about 30.

4. The process of claim 3 wherein R_4 is R_3 and R_4 is in a position ortho to the repeating oxyethylene grouping.

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U.S. Cl. X.R.

8—168, 171, 172; 117—76, 138.8, 139.5, 161