United States Patent Office 2,949,432 Patented Aug. 16, 1960

2,949,432

FIBER-FORMING COMPOSITION CONTAINING AN ACRYLONITRILE POLYMER PLASTICIZED WITH TRI-(2-ETHYLHEXYL) PHOSPHATE

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No Drawing. Filed Sept. 12, 1957, Ser. No. 683,456

4 Claims. (Cl. 260—30.6)

This invention relates to improved fiber-forming acrylonitrile polymer compositions and relates more particularly to fiber-forming acrylonitrile polymers which contain trialkyl phosphates and which have improved physical properties.

Acrylonitrile polymers containing more than about 80 percent acrylonitrile in the polymer have found many uses in the textile art. While these polymeric materials have had outstanding success in textile applications, improved compositions for use in applications such as carpeting have been desired. In carpeting, fibers with high single filament elongation at break, good resilience, resistance to matting and the like are desired.

Among the objects of this invention is the provision of an improved fiber-forming acrylonitrile polymer composition which may be formed into fibers having increased elongation, improved resilience and processing characteristics and decreased tendency to matting in carpets. Other objects of the invention will be apparent from the description which follows.

The objects of this invention are accomplished through the use of acrylonitrile polymers of more than 80 percent by weight acrylonitrile containing from about 5 to about 50 percent by weight of a trialkyl phosphate. These novel compositions in fiber form have improved elongation, improved processing characteristics, a decreased tendency to matting and improved resilience in carpeting; and, quite unexpectedly, in carpeting, improved flame resistance even when the trialkyl phosphate is present in the fiber in amounts as low as about 5 percent.

The successful use of trialkyl phosphates in fiber-forming acrylonitrile polymers was quite unexpected since the art is generally aware that the phosphate ester plasticizers generally are not compatible with and do not placticize acrylonitrile polymers, and even when special techniques are employed to mix phosphate ester plasticizers with acrylonitrile polymers, as by heating, the plasticizers will bleed out or exude at room temperature. Further, plasticizers are usually removed from the polymeric compositions in the wet spinning of fibers during the fiber-forming operation and washing process.

The most common organic phosphate ester plasticizer which has found wide use in plastics is tricresyl phosphate. Although some improvement in fiber physical properties is obtained when this material is incorporated into fiber-forming acrylonitrile polymer compositions, it was found that during the wet spinning of a composition containing solvent, the acrylonitrile polymer and tricresyl phosphate, that a large proportion of the tricresyl phosphate was extracted from the fiber during the spinning and washing process. This of course is particularly undesirable since the costly tricresyl phosphate is lost, the amount retained in the fiber varies and complication of the recovery process for solvent results. Of even less value were phosphoric esters of alkyl phenols and mixed cresyl diphenyl phosphates which were completely removed from the fibers during the wet spinning process.

Quite unexpectedly it was then found, contrary to experience with tricresyl phosphate, that trialkyl phosphates, when mixed in the solvent-acrylonitrile polymer mixture were not extracted from the fiber in the wet spinning operations. Extraction would have been expected by the man skilled in the art since trialkyl phosphates such as tri(2-ethylhexyl)phosphate are soluble in the usual acrylonitrile polymer solvents, as is tricresyl phosphate.

There are other advantages in the use of the trialkyl phosphates over tricresyl phosphate. For one, the solvent is more readily removed from the fiber during the processing steps subsequent to spinning when tri(2-ethylhexyl)phosphate is used, as compared to tricresyl phosphate. An added advantage is that carpeting made from acrylonitrile fiber compositions containing tri(2-ethylhexyl)phosphate resists soiling better than similar carpeting prepared from fiber materials containing tricresyl phosphate.

The trialkyl phosphates found useful in the practice of this invention contain from 6 to 16 carbon atoms in the alkyl groups and more preferably 8 to 10 or 12 carbon atoms in the alkyl groups as hydrocarbon radicals. Mixed esters, for example C_6, C_8, C_{10}, and mixed plasticizers are particularly advantageous in the invention. Examples of useful trialkyl phosphates include trihexyl phosphate, tridecyl phosphate, tri(2-ethylhexyl)phosphate, trioctyl phosphate, triisooctyl phosphate, hexyldioctyl phosphate and the like. The amount of trialkyl phosphate ordinarily may be varied from about 3 to 5 to about 50 percent based on the weight of the total polymer in the composition, but more preferably is varied from about 5 to about 30 weight percent trialkyl phosphate with about 95 to about 70 weight percent of the acrylonitrile polymers.

The polymeric materials which may be employed in the practice of the present invention are polyacrylonitrile; copolymers of acrylonitrile including binary and ternary polymers containing at least 80 weight percent of acrylonitrile in the polymer molecule and up to 20 weight percent of monomers copolymerizable therewith; or blends comprising polyacrylonitrile or copolymers comprising acrylonitrile, the blend having an overall polymerized acrylonitrile content of at least 80 percent by weight as will be set forth in more detail hereinafter.

For example, the polymer may be a copolymer of from 80 to 98 percent acrylonitrile and from 2 to 20 percent of another monomer containing the >C=C< linkage and copolymerizable with acrylonitrile. Suitable monoolefinic monomers include acrylic, alpha-chloroacrylic and methacrylic acids; the acrylates such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, octyl methacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromoethylene; methacrylonitrile; acrylamide and methacrylamide, alpha-chloroacrylamide or monoalkyl substitution products thereof; methyl vinyl ketone; vinyl carboxylates such as vinyl acetate, vinyl chloroacetate, vinyl propionate, and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and itaconic ester; N-vinylcarbazole; vinyl furane; alkyl vinyl ethers; vinyl sulfonic acid; ethylene alpha-, beta-dicarboxylic acids or their anhydrides or derivatives such as diethyl fumarate, diethyl maleate, diethyl citraconate, diethylmesaconate; styrene; vinyl nephthalene; acenaphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridines, for example, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine, etc., 1-vinyl-

imidazole and alkyl-substituted 1-vinylimidazoles, such as 2-, 4-, or 5-methyl-1-vinylimidazole, and other >C=C< containing copolymerizable materials.

The polymer may be a ternary interpolymer, for example, products obtained by the interpolymerization of acrylonitrile and two or more of any of the monomers, other than acrylonitrile, enumerated above. More specifically, a useful ternary polymer comprises acrylonitrile, methacrylonitrile, and 2-vinylpyridine. The ternary polymers may contain, for example, from 80 to 97 percent of acrylonitrile, from 1 to 10 percent of a vinylpyridine or a 1-vinylimidazole, and from 1 to 18 percent of another substance, such as methacrylonitrile or vinyl chloride.

The polymer may also be a blend of polyacrylonitrile or of an interpolymer of from 80 to 99 percent acrylonitrile and from one to 20 percent of at least one other >C=C< containing substance copolymerizable with acrylonitrile, with from 2 to 50 percent on the weight of the blend of a copolymer of from 10 to 70 percent of at least one other >C=C< containing polymerizable monomer. Preferably, when the polymeric material comprises a blend, it will be a blend of a copolymer of 90 to 98 percent of acrylonitrile and from 2 to 10 percent of another monoolefinic monomer, such as vinyl acetate, with a sufficient amount of a copolymer of from 10 to 70 percent of acrylonitrile or N-vinylcarbazole and the like and from 30 to 90 percent of a vinyl-substituted tertiary heterocyclic amine, such as vinylpyridine or 1-vinylimidazole, to give a dyeable blend having an overall vinyl-substituted tertiary heterocyclic amine content of from 2 to 10 percent, based on the weight of the blend.

The polymers useful in the practice of the present invention may be prepared by any conventional polymerization procedure, such as mass polymerization methods, solution polymerization methods, or aqueous emulsion procedures. The preferred practice utilizes suspension polymerization wherein the polymer is prepared in finely divided form for immediate use in the fiber fabrication operations. The preferred suspension polymerization may utilize batch procedures wherein monomers are charged with an aqueous medium containing the necessary catalyst and dispersing agents. A more desirable method involves the semi-continuous procedure in which the polymerization reactor containing the aqueous medium is charged with the desired monomers gradually throughout the course of the reaction. Entirely continuous methods involving the gradual addition of monomers and the continuous withdrawal of polymer may also be employed.

The most effective polymers for the preparation of fibers are those of uniform physical and chemical properties and of relatively high molecular weight. The polymers should have molecular weights of at least about 10,000 and preferably between about 25,000 and 150,000.

In preparing the products of the present invention, conventional equipment ordinarily employed in the manufacture of artificial and synthetic fibers and filaments may be used and particularly the equipment which is usually employed in the manufacture of fibers and filaments from acrylonitrile polymers. The present invention is applicable to the usual methods for forming synthetic filaments and fibers, such as dry spinning and wet spinning. However, for the purposes and importance of the process, the invention will be described as it is applicable to the wet spinning technique. It will be understood that in dry spinning the trialkyl phosphate is intimately blended in the polymer prior to spinning.

In the wet spinning process, a solution of the polymer and trialkyl phosphate, commonly referred to as the "dope," is first prepared. Solvents for the acryonitrile polymers include N,N-dimethylacetamide; N,N-dimethylformamide; nitromethane and water; tris(dimethylamido)phosphate; N-nitrosopiperidine; mixtures of ethylene sulfite with N,N-dimethylacetamide, N,N-dimethylformamide, and nitromethane and water; tri(betacyanoethyl)nitromethane; trichloronitropropanol; mixtures of diethyl phosphate and N,N-dimethylacetamide and N,N-dimethylformamide, and the like; and such solvents as dimethyl methanephosphonate, gamma-butyrolactone, ethylene carbonate and the like.

The "dope" is extruded through an orifice or a plurality of orifices in the face of a spinnerette submerged in a coagulating medium or bath. The bath comprises a non-solvent for the polymer which is also a solvent for or miscible with the solvent in the "dope." The coagulating medium or bath will comprise an aqueous solution of a solvent for the polymer being spun, the concentration of the bath being such that the solvent becomes a nonsolvent for the polymer. For example, in the case of amides such as N,N-dimethylformamide, N,N-dimethylacetamide, and the like, an aqueous coagulating bath containing 1 to 75 percent of the amide is satisfactory.

The filament or filaments are removed from the coagulating bath and passed through a washing medium where all residual solvent and coagulating liquid are removed therefrom. Water is the preferred washing medium and is usually contained in a bath through which the filaments are passed. In the bath the washing medium may flow concurrent or countercurrent to the direction of travel of the filaments therethrough. Washing rolls or like apparatus may also be employed, if desired. Thereafter the filaments are dried and steam stretched, if desired.

In order to orient the polymer molecules in the filaments and particularly if no steam stretch is to be given, they are stretched while in the washing bath or coagulating bath or in both. Further, a solvent stretch bath may be employed immediately following the coagulating bath wherein the polymer molecules in the filaments are oriented. It is to be noted, however, that the conditions of the bath where the stretching is to be done, such as temperature, size, length of time that filament remains therein, etc., are so regulated as to prevent crystallization of the polymer. Normally, the solvent stretch or wash bath is maintained at a temperature in the range of 80° to 100° C. and the filaments remain therein for a period less than 15 seconds.

Any solvent for acrylonitrile polymers may be employed in the solvent stretch bath which may comprise a series of stages. The concentration of the solvent in the bath will depend upon the chemical characteristic of the solvent used and the temperature of the bath. Obviously, the concentration must be such that the polymer article passing therethrough will not dissolve therein. Certain solvents may be used in higher concentrations than others. For example, up to 100% N,N-dimethylacetamide may be employed. Usually, however, a solvent stretch bath containing from about 10 to 85% solvent by weight, such as N,N-dimethylacetamide, N,N-dimethylformamide, and the like, is satisfactory for the purposes of the instant invention. The bath may contain varying concentrations of solvent at different stages during the stretching steps.

During the coagulating and washing step the conditions of time and temperature are maintained so as to prevent crystallization of the filaments. Then the filaments are crystallized while in a relaxed condition. Thereafter the fibers are dried and cut into staple fibers, when the same is desirable. Alternatively, the filaments may be dried and cut into staple fibers under such conditions that crystallization does not take place and then relaxed and crystallized.

The following specific embodiment is illustrative of the improved products of this invention.

A spinning solution or "dope" was prepared by mixing together 23.2 kilograms of an acrylonitrile polymer, 100 kilograms of N,N-dimethylacetamide and 175 grams of titanium dioxide. To this slurry there was then added 5.8 kilograms of tri(2-ethylhexyl) phosphate and the slurry heated to dissolve the polymer in the solvent. The

tri(2-ethylhexyl)phosphate may also be added to the "dope" after the polymer is put into solution by heating, and the titanium dioxide may be omitted if bright fibers are desired. The acrylonitrile polymer was a blend of (A) a copolymer of 94 percent acrylonitrile and 6 percent vinyl acetate and (B) a copolymer of 50 percent acrylonitrile and 50 percent 2-methyl-5-vinylpyridine, said blend containing 6 percent methyl vinylpyridine based on the total weight of the blend. The "dope" was filtered and forced through a spinnerette containing 5,000 holes into a coagulating bath containing water and a slight excess of dimethylacetamide. After coagulation, the fibers in the form of filaments or tow are stretched and washed, dried, annealed and crimped by standard methods known to those in the art. The resulting fiber product contained 97 percent (24.3%) of the tri(2-ethylhexyl)phosphate used in the "dope" originally, as determined by chemical analysis. A similar fiber composition prepared with tricresyl phosphate contained less than about 65 percent of the tricresyl phosphate originally in the spinning "dope." The remainder of the tricresyl phosphate was washed out in the coagulation bath and washing process. As shown by chemical analysis, the residual solvent in the fiber was much less in the case of tri(2-ethylhexyl) phosphate than that in fibers containing tricresyl phosphate showing that the solvent is more readily removed from fibers containing tri(2-ethylhexyl)phosphate than tricresyl phosphate.

4 ply 4s cotton count yarn was made from the two fibers described above and a 9 stitch, 3/16th gauge, 3/8 inch loop carpet with a synthetic rubber latex backing was made by conventional textile techniques. In preparing this carpeting, the improved processing characteristics of fibers containing tri(2-ethylhexyl)phosphate was readily apparent. The resulting carpeting had excellent resiliency and good resistance to matting. The carpeting made from the fiber containing tri(2-ethylhexyl)phosphate resisted soiling much better than similar carpeting prepared from the fiber materials containing equivalent amounts of tricresyl phosphate.

The carpeting made with the fiber containing tri(2-ethylhexyl)phosphate was tested for flame resistance by the following procedure: a portion of the carpet was put in a small box-like enclosure and ten wooden kitchen matches were lighted and dropped on the capet, none of the ten matches caused the carpet to burn. When a similar test was applied to carpet made from the same fiber as described above without the added tri(2-ethylhexyl)phosphate, all ten matches caused burning of the carpet. Carpeting was also prepared from a 50/50 fiber blend of the fiber described above containing tri(2-ethylhexyl)phosphate and the fiber without tri(2-ethylhexyl) phosphate. This carpeting also did not burn under the test conditions described above.

When the above embodiment of the invention is repeated with tri(2-ethylhexyl)phosphate in amounts of 5, 10, 15, 20 and 30 percent based on the total fiber composition, similar excellent results are obtained. Fibers containing 10 percent tri(2-ethylhexyl)phosphate of 15.6 denier had a tenacity 1.75 g./d. and 45 percent elongation. Fibers which did not contain tri(2-ethylhexyl)phosphate of 15.8 denier had a tenacity of 1.8 and 36.8 percent elongation. Equivalent excellent results are also obtained when other trialkyl phosphates such as tridecyl, trioctyl and the like are employed. Use of other fiber-forming acrylonitrile polymers such as polymers were (B) is a copolymer of N-vinylcarbazole and vinylpyridine; and from polymers of 93 percent acrylonitrile and 7 percent vinyl acetate also result in improved polymer and fiber products.

Numerous other embodiments will be evident to those skilled in this art which are within the scope of this invention.

We claim:

1. A plasticized fiber-forming composition of matter adapted to be spun into filaments by the wet spinning process without substantial loss of the plasticizer, comprising a polymer containing at least 80 weight percent of acrylonitrile and another monoolefinic monomer copolymerized therewith and tri-(2-ethylhexyl)phosphate as the plasticizer, said composition of matter containing 5 to 50 percent of said phosphate based on the weight of said phosphate and said polymer.

2. The composition of matter of claim 1 dissolved in N,N-dimethylacetamide.

3. The composition of matter of claim 2, wherein the polymer is an acrylonitrile polymer containing 90 to 97 weight percent acrylonitrile and 10 to 3 weight percent vinyl acetate.

4. The composition of matter of claim 2 wherein the polymer is a blend of a copolymer of 80 to 99 weight percent acrylonitrile and up to 20 weight percent of another monoolefinic monomer copolymerized therewith and a copolymer of 10 to 70 weight percent acrylonitrile and 90 to 30 weight percent of 2-methyl-5-vinylpyridine, said blend having an overall vinylpyridine content of from 2 to 10 weight percent based on the weight of the blend.

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