Flame-retardant acrylic synthetic fibers containing a fluid mixture obtained by dissolving halogen- and/or phosphorus-containing solid organic compounds in a liquid halogenated aliphatic phosphate.

9 Claims, No Drawings
FLAME-RETARDANT ACRYLIC SYNTHETIC FIBERS HAVING IMPROVED PROPERTIES

The present invention relates to flame-retardant acrylic synthetic fibers with improved chemical and physical properties, and also to a method for producing such acrylic synthetic fibers. More particularly, in producing flame retardant acrylic synthetic fibers containing a liquid halogenated aliphatic phosphate, the present invention relates to a method for improving the various properties of the fibers such as touch, luster, anti-fibrillation property, heat-settability, resilience, etc. and for augmenting the flame retardant property of the fibers to a further extent as well as for preventing the fluctuation in dyeability, characterized in that a fluid mixture having a viscosity of at least 6,000 centipoises at 25°C obtained by dissolving in the halogenated aliphatic phosphate a solid organic compound which is soluble in the halogenated aliphatic phosphate and contains halogen and/or phosphorus, is introduced into the fibers.

It is well known that acrylic synthetic fibers can be rendered flame retardant by introducing a halogenated aliphatic phosphate into the fibers. When a proper amount of a halogenated aliphatic phosphate is introduced into the fibers, the resultant fibers certainly show not only desirable flame retardant property but also good touch, good luster and other good properties. However, if the halogenated aliphatic phosphate to be introduced into the fibers is increased to such an amount as to make the fibers more flame-retardant, the flame retardant property is further improved, but other fiber qualities and properties will deteriorate with the increase of the amount of the flame retardant additive. Therefore, the various disadvantages resulting from the halogenated aliphatic phosphate introduced into the fibers, such as the fibrillation caused in the steps of forming the fibers containing the halogenated aliphatic phosphate, lack in resilience of the products in use, change of touch with the passage of time, etc. were inevitable when a large amount of the halogenated aliphatic phosphate was introduced.

The above-mentioned phenomenon can be more concretely explained from the following fact: Thus, by introducing the above-mentioned halogenated aliphatic phosphate into the fibers, it is possible to obtain acrylic synthetic fibers for use in artificial hair having excellent touch and luster like human hair and a flame retardant property. However, when the fibers are sewed by machine in the step of preparing hair products or when the products in use are combed or brushed, there will be formed undesirable fibrillated, branched or worn-out hair, or when the products are washed the curls and waves of the artificial hair tend to vanish. Therefore, in such products there is a problem of deteriorating the excellent touch and luster of the fibers like human hair with the passage of time during wearing. It is also a problem that the products are not durable to a long time wear because of the lack in resilience of the curls and waves or the loss of resilience with the passage of time.

In order to avoid the disadvantages of deterioration of the fiber qualities and properties resulting from introducing a large amount of the above mentioned flame retardant additive into the fibers, attempts have been made to reduce the amount of the halogenated aliphatic phosphate to be added to the fibers by using, to-
3,846,373

causing fibrillated, branched or worn out hair upon combing or brushing, and of tending to lose the curls and waves by washing, i.e., free from the changes in the excellent human hair-like touch and luster with the passage of time during wearing.

It is to be noted that the acrylic synthetic fibers according to the present invention shows a much higher flame retardant property than that of the conventional acrylic synthetic fibers containing only a halogenated aliphatic phosphate when the amount of the flame retardant additive incorporated into the fibers is the same.

It is also to be noted that the acrylic synthetic fibers obtained according to the present invention do not show any fluctuations in dyeability as contrasted to the conventional acrylic synthetic fibers containing only a halogenated aliphatic phosphate.

Additionally, the flame retardant acrylic synthetic fibers obtained according to the present invention, when used for preparing artificial hair, can give more excellent human hair-like luster, by using a compound having a refractive index at 25°C ranging from 1.44 to 1.60 as the above-mentioned halogenated aliphatic phosphate.

The halogenated aliphatic phosphate to be used in this invention and represented by the above indicated general formula include liquid compounds such as tris(2-chloroethyl)phosphate, tris(2-bromoethyl)phosphate, tris(3-chloropropyl)phosphate, tris(3-bromopropyl)phosphate, chloropropylphosphate, tris(2-bromopropyl)phosphate, tris(2,3-dichloropropyl)phosphate, tris(2,3-dibromopropyl)phosphate, tris(1-bromo-3-chloroisopropyl)phosphate, tris(2,3-dichlorobutyl)phosphate, tris(2,3-dibromobutyl)phosphate, bis(2,3-dichloropropyl) 2,3-dibromopropylphosphate, bis(2,3-dibromopropyl)2,3-dichloropropylphosphate, etc.

The solid organic compounds containing halogen and/or phosphorus and soluble in the above-mentioned halogenated aliphatic phosphate are those which are solid at room temperature. Examples thereof are halogenated paraffins such as chlorinated paraffins, brominated paraffins; halogenated aralkyl or aryl phosphates (preferably having not more than 20 carbon atoms) such as tris(bromocresyl)phosphate, tris(dibromophenyl)phosphate, etc.; tetrabromobisphenol-A or its etherified derivatives represented by the following general formula:

\[
\begin{align*}
R_1 & \quad O \\
C & \quad I \\
C_2H_5 & \quad Br \\
R_2 & \quad OR_2
\end{align*}
\]

wherein each of \(R_1\) and \(R_2\) is alkyl, cycloalkyl, aralkyl or aryl group which is unsubstituted or substituted with halogen atom(s) and which has 2 to 20 carbon atoms, such as bis(benzyl)ether of tetrabromobisphenol-A, bis(chlorobromopropyl)ether of tetrabromobisphenol-A, etc.; precodensates of tetrabromobisphenol-A with polyhalogenated compounds or diepoxides, etc.; halogenated diphenyl ethers such as chlorinated diphenyl ether, brominated diphenyl ether, etc.; halogenated phenols or its halogenated alkyl (preferably not more than 10 carbon atoms) ethers, etc. Besides these, any other solid organic compounds containing halogen and/or phosphorus and soluble in the halogenated aliphatic phosphate can be used.

Such a halogenated aliphatic phosphate and an organic compound containing halogen and/or phosphorus may be mixed in various combinations and dissolved to form a homogeneous fluid mixture having a viscosity of at least 6,000 centipoises. Any mixing ratio (by weight) of such a halogenated aliphatic phosphate and such organic compounds containing halogen and/or phosphorus can be used, if this ratio gives a fluid mixture satisfying the foregoing viscosity. However, in general, it is desirable to use a ratio within the range of from 9.5:0.5 to 0.5:9.5, preferably 9/1–3/7.

By the term “fluid mixture” as used herein is meant a homogeneous composition which is fluid at room temperature or upon the operation of introducing the mixture into the fibers. Also, it is an essential requirement that the viscosity of the fluid mixture should be at least 6,000 centipoises at 25°C. When a fluid mixture of less than that viscosity is used, it is difficult to fully attain the objects of the present invention. The upper limit of the viscosity of the fluid mixture according to the present invention may vary depending on the particular combination of the halogenated aliphatic phosphates and the organic compound containing halogen and/or phosphorus to be used or on the degree of the desired modifying effect of the fiber. Even a composition which is solid at room temperature but is fluid upon introducing it into the fibers can be used. However, a viscosity of less than 300,000 centipoises is generally desirable for operation.

By introducing such a fluid mixture into the fibers in an amount of not less than 3 percent on the weight of the fibers, it is possible to obtain acrylic synthetic fibers having a high flame retardant property and improved properties in various other respects. In general, the upper limit of the amount of the fluid mixture to be introduced into the fibers is desirable to be not to be more than 40 percent in consideration of the other fiber properties.

The most advantageous procedure to introduce such a fluid mixture of halogenated aliphatic phosphate and organic compounds containing halogen and/or phosphorus into the acrylic synthetic fibers is to incorporate a fluid mixture having a viscosity within the above-mentioned specified range into the spinning solution for producing the fibers. Then the spinning solution containing said fluid mixture is formed into filaments by a generally well known wet spinning or dry spinning method. The spun filaments may further be treated in a known manner. Thus, the filaments may be water-washed, stretched, dried and heat-treated. Another procedure for causing the above-mentioned fluid mixture to be contained in the fibers is to treat the gel filaments (obtained by dry- or wet-spinning an acrylic polymer solution through spinneret orifices under general spinning conditions) in a treating bath containing a fluid mixture of a viscosity within the above-mentioned specified range, and then to carry out the usual post treatment steps. Thus there can be various procedures to cause the above-mentioned halogenated aliphatic phosphate and organic compound containing halogen and/or phosphorus to be contained in the fibers according to the present invention. By any of these
procedures, the objects of the present invention can be satisfactorily attained so far as a specified amount of the fluid mixture of the present invention can be incorporated into the acrylic synthetic fibers.

Various kinds of spinning solution containing an acrylonitrile polymer dissolved in a suitable solvent, which can be used in producing the acrylic synthetic fibers of the present invention are well known in the art. Representatives of such polymers and solvents are disclosed in the specification of U.S. Pat. No. 2,948,581 granted to Cumming on Aug. 9, 1960 and other U.S. Patents cited therein.

The representative compounds which may be copolymerized with acrylonitrile to produce acrylonitrile polymers useful for the practice of the present invention are those containing one

$$\text{CH}_2=\text{C} < \text{radical}.$$ 

Such compounds include, for example, vinyl esters of saturated aliphatic carboxylic acids such as vinyl acetate, vinyl propionate, vinyl butyrate, etc.; vinyl halides and vinylidene halides such as vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene bromide, vinylidene fluoride; allyl type alcohols such as allyl alcohol, methallyl alcohol, ethallyl alcohol, etc.; allyl, methallyl and other unsaturated alcohol ester of monobasic acids such as allyl or methallyl acetate, laurate, cyandate, etc.; acrylic acid, alkacylic acids (such as methacrylic acid, ethacylic acid, etc.), and esters and amides of such acids (such as methyl, ethyl, propyl, butyl acrylates and methacrylates; acrylamide, methacrylamide, N-methyl, -ethyl, -propyl, -butyl acrylamides and methacrylamides); methacyronitrile, ethacylonitrile, and other hydrocarbon substituted acrylonitriles; unsaturated sulfonic acids having one

$$\text{CH}_2=\text{C} < \text{radical}$$

and their salts such as allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid and their sodium salts and potassium salts; unsaturated aliphatic hydrocarbon having one

$$\text{CH}_2=\text{C} < \text{radical}$$

such as isobutylene; many other vinyl, acrylic and other compounds having one

$$\text{CH}_2=\text{C} < \text{radical}$$

which polymerize with acrylonitrile to produce thermoplastic copolymers. Alkyl esters of $\alpha, \beta$-unsaturated polycarboxylic acids such as dimethyl, -ethyl, -propyl, -butyl esters of maleic acid, fumaric acid, citraconic acid also copolymerize with acrylonitrile to form copolymers.

Usually, the molecular weight (average molecular weight) of the acrylonitrile homopolymer or copolymer for producing polycyronitrile shaped products is within the range of from 25,000 or 30,000 to 200,000 or 300,000, or higher, and the particularly advantageous range is from 50,000 to 100,000. These molecular weights are calculated from the viscosity of the polymer in dimethylformamide calculated by the Staudinger's equation (refer to the specification of U.S. Pat. No. 2,404,713 dated June 23, 1946.).

 Preferably, the acrylic polymer to be used in this invention is an acrylonitrile homopolymer or copolymer containing 30 percent or less of at least one of the above mentioned monothioynamically unsaturated monomer and at least 70 percent acrylonitrile, but polymers containing a less amount of acrylonitrile may also be used for the practice of the present invention.

The representative solvents which are useful to dissolve the acrylonitrile polymer to prepare the spinning solution include organic solvents such as dimethylformamide, dimethylacetamide, ethylene carbonate, and diethyl sulfoxide, and inorganic solvents such as concentrated aqueous solution of inorganic salts, for example sodium thiocyanate, zinc chloride, etc.

The spinning methods used for obtaining the fibers of the present invention may be the generally known wet or dry spinning processes described in Japanese Patent Nos. 3645/50, 4821/53, 9516/57, 878/63 and 2589/61, and U.S. Pat. Nos. 2,404,725 to 2,404,728.

The following examples are for better explanation of the present invention and are not intended to limit the scope of the invention. All the percentages and parts in the examples are by weight unless otherwise indicated.

**EXAMPLE 1**

A fluid mixture having a viscosity of 230,000 centipoises at 25°C consisting of 70 parts tris(1-bromo-3-chloroisopropyl)phosphate having a viscosity of about 3,000 centipoises at 25°C and 30 parts chlorinated paraffin containing 70 percent chlorine was prepared. The fluid mixture was then added to a spinning solution composed of 11 parts of a copolymer consisting of 88 percent acrylonitrile and 12 percent vinyl acetate and 89 parts of a 44 percent aqueous solution of sodium thiocyanate, the amount of the fluid mixture being 40 percent on the basis of the weight of the polymer. Thereafter, the fluid mixture was thoroughly dispersed in the spinning solution by a high shear mixer (Homomixer SL Type, manufactured by Tokushu Kika Co., Japan). Thus thus-obtained spinning solution was then extruded through a spinneret having eight orifices of each 0.2 mm in diameter into a 12 percent aqueous solution of sodium thiocyanate at -2°C. The formed filaments were stretched ten times the original length in hot water, washed with water and then steam-relaxed at 110°C to obtain acrylic synthetic fibers of 50 denier per filament.

The thus-obtained acrylic synthetic fibers were evaluated for flammability to show extremely high self-extinguishability. Further, no fibrillation was observed upon dyeing, cutting and sewing the fibers to prepare artificial hair products.

For comparison, when tris(1-bromo-3-chloroisopropyl)phosphate was singly introduced into the fibers instead of the above-mentioned fluid mixture, the flame-resistance of the thus-obtained fibers was observed to be much inferior to that of the fibers according to the present invention. Furthermore, in the sewing step for producing artificial hair products, the
fibers in contact with the sewing machine turned white, which showed the occurrence of fibrillation.

**EXAMPLE 2**

In table 1 are shown several properties of various acrylic synthetic fibers obtained by the method as shown in Example 1 in which various amounts of the conventional flame retardant additive tris(1-bromo-3-chloroisopropyl) phosphate singly as well as a homogeneous fluid mixture having a viscosity of 24,400 centipoises at 25°C consisting of 70 percent said phosphate and 30 percent bis(2,3-dibromopropyl)ether of tetrabromobisphenol A were introduced into the fibers.

As apparent from the results in Table 1, it is observed that, by the method of the present invention, the acrylic synthetic fibers containing the conventional halogenated aliphatic phosphate can be remarkably improved in the fiber properties including the flame retardant property and dyeability.

In the above table the flammability was determined by filling 4 g. of the fibers into a metal wire basket (6.5 cm. in diameter and 7.5 cm. in height), and contacting a burner flame to the bottom of the basket for 7 seconds. The burning time and burnt off weight were measured. The fibrillation was determined as follows. Thus a bundle of 800 monofilaments (40 cm. in length) was subjected to 200 times brushing and the number of fibrillated monofilaments was counted. The dyeability was determined as follows. Thus the fibers were dyed under the following conditions:

<table>
<thead>
<tr>
<th>Cationic dye</th>
<th>C.I. Basic Orange 21 (C.I. 48035)</th>
<th>2% o.w.f.</th>
<th>Cationic retarder:</th>
<th>0.3% o.w.f.</th>
<th>Acetic acid:</th>
<th>10% o.w.f.</th>
<th>Liquor ratio:</th>
<th>1/100</th>
<th>Temperature:</th>
<th>Increased from 60°C to 100°C at a rate of 1°C/min. and maintained at 100°C for 45 min.</th>
</tr>
</thead>
</table>

After dyeing, the presence of uneveness in dyeing was observed.

<table>
<thead>
<tr>
<th>Introduction of halogenated aliphatic phosphate only</th>
<th>Content of additive</th>
<th>Flammability</th>
<th>Fibrillation</th>
<th>Stickiness</th>
<th>Unevenness in dyed colors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction of the same after being formed into the fluid mixture of the present invention</td>
<td>28%</td>
<td>17</td>
<td>33%</td>
<td>Observed</td>
<td>Observed</td>
</tr>
<tr>
<td>26</td>
<td>52</td>
<td>77</td>
<td>Observed slightly</td>
<td>Observed slightly</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>59</td>
<td>81</td>
<td>Observed slightly</td>
<td>Observed slightly</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>3</td>
<td>29</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>3</td>
<td>23</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>2</td>
<td>24</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLE 3**

Tris(1-bromo-3-chloroisopropyl)phosphate, which is a halogenated aliphatic phosphate flame retardant additive, was added to an acrylic spinning solution composed of 11 parts of a copolymer consisting of 90 percent acrylonitrile and 10 percent methylacrylate and 89 parts of 44 percent aqueous solution of sodium thiocyanate such that the flame retardant additive is 20 percent based on the weight of the copolymer. Thereafter, the flame retardant additive was dispersed in the spinning solution thoroughly by a high shear mixer. The thus-obtained spinning solution was then extruded into a 12 percent aqueous solution of sodium thiocyanate at −2°C through a spinneret having 50 orifices of each 0.2 mm in diameter. The formed filaments were stretched 10 times the original length in hot water, washed with water and then steam-relaxed at 115°C to obtain acrylic synthetic fibers of three denier per filament. After combing the thus-obtained fibers 500 times, considerable fibrillation was observed.

On the other hand, a fluid mixture having a viscosity of 6,800 centipoises at 25°C consisting of 10 parts of the above-mentioned flame retardant additive and 30 parts of pentabromobiphenyl ether was prepared. This fluid mixture was used instead of the above-mentioned flame retardant additive, and acrylic synthetic fibers of three denier per filament were obtained in the same way. After combing the thus-obtained fibers, no substantial fibrillation was observed even after 500 times combing.

The same procedure was repeated except that a fluid mixture having a viscosity at 25°C of 36,000 centipoises and consisted of 70 percent of tris(1-bromo-3-chloroisopropyl)phosphate and 30 percent of bis(β-bromoethyl)ether of tetrabromobisphenol-A was used as the fluid to be added to the spinning solution. The resultant fibers were excellent in flame-retardancy, hand (touch), lustre and even dyeability as compared with the fibers obtained by the use of each of the above two compounds singly.

**EXAMPLE 4**

A fluid mixture having a viscosity at 25°C of 46,000 centipoises and consisting of 70 percent of bis(2,3-dichloropropyl)2,3-dibromopropyl phosphate and 30 percent of bis (β-bromoethyl) ether of tetrabromobisphenol-A was added to an acrylic spinning solution consisting of 11 parts of an acrylic copolymer (92 percent acrylonitrile and 8 percent vinyl acetate) and 89 parts of a 44 percent aqueous solution of sodium thiocyanate, the amount of the fluid mixture being 10 percent based on the copolymer in the spinning solution. Then the fluid mixture was fully dispersed in the spin-
ning solution by the use of a high shear mixer. The spinning solution was extruded through a spinneret (50 holes, each 0.09 mm in diameter) into a 12 percent aqueous solution of sodium thiocyanate at -2°C to form filaments. The filaments were stretched 10 times the length, washed with water and steam-relaxed at 120°C to obtain acrylic fibers (referred to as A) having 3 denier per monofilament.

For comparison, the same procedure was repeated except that bis(2,3-dichloropropyl)2,3-dibromopropyl phosphate alone or bis(β-bromoethyl)ether of tetrabromobisphenol-A alone was used as the additive for the spinning solution to obtain fibers B or fibers C respectively.

In respect of these fibers A, B and C flammability was evaluated in the same manner as in Example 2. It was observed that the fibers A are far more excellent in flame-retardancy than the fibers B and C. Further the fibers B had a somewhat sticky hand and the fibers C were extremely delustered and tended to fibrillation, but the fibers A of this invention were not sticky, excellent in hand and lustre and had no tendency to fibrillation.

The same procedure was repeated except that a fluid mixture having a viscosity at 25°C of 9,200 centipoises and consisting of 70 percent of tris(2,3-dibromopropyl) phosphate and of 30 percent bis(β-bromoethyl)ether of tetrabromobisphenol-A was used as the fluid to be added to the spinning solution. The resultant fibers were excellent in flame-retardancy, hand, lustre, anti-fibrillation, etc. as compared with the fibers obtained by the use of each of the above two compounds singly.

What we claim is:

1. A flame-retardant monocomponent acrylic synthetic fiber comprising an acrylonitrile polymer selected from the group consisting of homopolymers of acrylonitrile and copolymers containing at least 70 percent acrylonitrile and up to 30 percent of at least one monothiocyanically unsaturated monomer copolymerized therewith, and having incorporated in such fibers 3-40 percent by weight of a fluid mixture having a viscosity of at least 6,000 centipoises at 25°C obtained by dissolving (1) an organic compound selected from the group consisting of halogenated paraffins, halogenated alkyphosphates, halogenated ary phosphates, halogenated diphenyl ethers, halogenated phenols, halogenated alkyl ethers of the halogenated phenols, tetrabromobisphenol-A and etherified derivatives of tetrabromobisphenol-A represented by the formula

\[
\begin{align*}
R_1O & \\
\text{Br} & \text{O} \\
\text{Br} & \text{O} \\
\text{CH}_3 & \text{OR}_2 \\
\end{align*}
\]

wherein each of \( R_1 \), \( R_2 \), respectively, represents alkyl, cycloalkyl, aralkyl or aryl which are unsubstituted or substituted by halogen, said \( R_1 \) and \( R_2 \) groups respectively having 2-20 carbon atoms, in (2) a liquid halogenated aliphatic phosphate represented by the formula

\[
R_1O \quad P = O \\
R_2O \\
R_3O
\]

wherein each of \( R_1 \), \( R_2 \) and \( R_3 \) represents a halogenated aliphatic hydrocarbon radical having up to eight carbon atoms.

2. The acrylic synthetic fiber of claim 1 wherein said fluid mixture has a viscosity of up to 300,000 centipoises at 25°C.

3. The acrylic synthetic fiber of claim 1 wherein the mixing ratio of the halogenated aliphatic phosphate and the organic compound in said fluid mixture is within the range of from 9.5:0.5 to 0.5:9.5 by weight.

4. The acrylic synthetic fiber of claim 3 wherein said mixing ratio is within the range of from 9:1 to 3:7 by weight.

5. The acrylic synthetic fiber of claim 1 wherein said halogenated aliphatic phosphate is a liquid having a refractive index of 1.44 to 1.60 at 25°C.

6. The acrylic synthetic fiber of claim 1 wherein said halogenated aliphatic phosphate is selected from the group consisting of tris(β-chloroethyl)phosphate, tris(β-bromoethyl)phosphate, tris(3-chloropropyl)phosphate, tris(3-bromopropyl)phosphate, tris(2,3-dichloropropyl)phosphate, tris(2,3-dibromopropyl)phosphate, tris(1-bromo-3-chloroisopropyl)phosphate, tris(2,3-dichlorobutyl)phosphate, tris(2,3-dibromobutyl)phosphate, bis(2,3-dichloropropyl)2,3-dibromopropyl phosphate and bis(2,3-dibromopropyl)2,3-dichloropropyl phosphate.

7. The acrylic synthetic fiber of claim 1 wherein said fluid mixture consists essentially of tris(1-bromo-3-chloroisopropyl)phosphate and bis(β-bromoethyl)ether of tetrabromobisphenol-A.

8. The acrylic synthetic fiber of claim 1 wherein said fluid mixture consists essentially of tris(1-bromo-3-chloroisopropyl)phosphate and bis(β-bromoethyl)ether of tetrabromobisphenol-A.

9. The acrylic synthetic fiber of claim 1 wherein said fluid mixture consists essentially of tris(2,3-dibromopropyl)phosphate and bis(β-bromoethyl)ether of tetrabromobisphenol-A.