United States Patent Office

3,660,351

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3,660,351

FLAME RESISTANT ACRYLONITRILE POLYMERS

Richard Frederick Schmidt, Stamford, and Joseph Jacinto Pellon, New Canaan, Conn., assignors to American Cyanamid Company, Stamford, Conn.

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Int. Cl. C08f 45/58

U.S. Cl. 260—45.85 8 Claims

ABSTRACT OF THE DISCLOSURE

An acrylonitrile polymer such as an acrylonitrile fiber having improved flame resistance contains a halogenated aromatic compound having the formula

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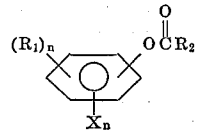

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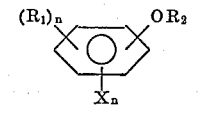

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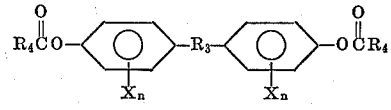

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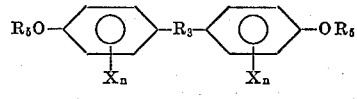

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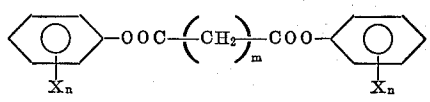

wherein R_1 is hydrogen, chlorine, bromine or an alkyl radical having from 1 to 9 carbon atoms, R_2 is an alkyl radical having 1 to 22 carbon atoms and the sum of the carbon atoms of R_1 and R_2 is greater than 9, R_3 is methylene, isopropylidene, oxygen or sulfur; R_4 is an alkyl radical containing at least one carbon atom; R_5 is a 2,3-dibromopropyl group; X is bromine or chlorine; *m* is an integer of from 0 to 22 and *n* is an integer of from 0 to 4 with the proviso that each formula contains at least two aromatically bound halogen atoms.

This invention relates generally to acrylonitrile polymers and more particularly to acrylonitrile polymers having improved flame resistance.

Fibers of acrylonitrile polymers are used extensively in various home furnishings such as carpets, draperies, upholstery and the like. To be entirely acceptable, the home furnishings must be flame resistance or self-extinguishing. While it is relatively easy to provide temporary flame resistance, it has been found to be very difficult to provide permanent protection. The more successful processes heretofore proposed have involved adding halogen bearing aliphatic compounds to the solution from which the fibers are spun. By selecting a hologenated aliphatic compound which is soluble in organic solvents, it is possible to improve to some extent the flame resistance of fibers spun from organic solvent solutions of the polymer. However, it is often preferred to wet spin the acrylonitrile fiber from a concentrated aqueous saline solution of the polymer. Experience has shown that when liquid halogenated aliphatic compounds such as tris (2,3-dibromopropyl) phosphate, halo-aliphatic acid esters,

halogenated paraffines, oils and the like are dispersed in the saline spinning solution, a large amount thereof is lost during spinning and subsequent dyeing of the fiber. While this loss can be somewhat reduced by using finely divided, solid, high melting halo-aliphatic compounds which become entrapped in the fiber matrix, such compounds also tend to reduce the luster of the fiber.

It is, therefore, an object of this invention to provide an improved flame resistance acrylonitrile polymer. Another object of the invention is to provide shaped, lustrous and flame resistant acrylonitrile polymers. Still another object of the invention is to provide shaped acrylonitrile polymers prepared from saline solutions thereof which have improved flame resistance. A still further object of the invention is to provide a process for making flame resistant shaped acrylonitrile polymers by wet spinning saline solutions of the polymer.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing shaped acrylonitrile polymers containing a halogenated aromatic compound having a melting point below about 100° C. and having one of the formula

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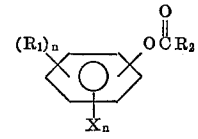

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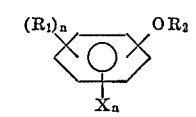

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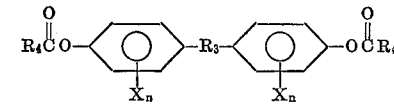

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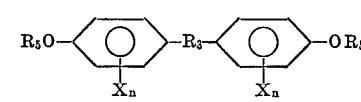

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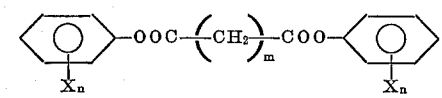

wherein R_1 is hydrogen, chlorine, bromine or an alkyl radical having from 1 to 9 carbon atoms; R_2 is an alkyl radical having 1 to 22 carbon atoms and the sum of the carbon atoms of R_1 and R_2 is greater than 9; R_3 is methylene, isopropylidene, oxygen or sulfur; R_4 is an alkyl radical containing at least one carbon atom; R_5 is a 2,3-dibromopropyl group; X is bromine or chlorine; *m* is an integer of from 0 to 22 and *n* is an integer of from 0 to 4 with the proviso that each formula contains at least two aromatically bound halogen atoms. R_1 may be, for example, methyl, ethyl, hexyl, nonyl or the like. R_2 and R_3 may be, for example, methyl, ethyl, butyl, octyl, octadecyl or the like. It has been found that a fiber of an acrylonitrile polymer having improved flame resistance can be produced without substantial deleterious effect upon the luster thereof by substantially uniformly mixing with a saline solution of the polymer one of the halogenated aromatic compounds of the above formulae, or mixtures thereof, and spinning the resulting mixture into an aqueous coagulating bath. The halogenated aromatic compounds dispersed in the spinning solution in accordance with this invention are not removed from the fiber during spinning or in subsequent dyeing steps in sufficient quantity to effect significantly the flame resistant properties of

the fiber. In fact, more than 90 percent of the halogenated compound dispersed in the spinning solution often remains in the fiber after spinning and dyeing.

The flame retardant compounds of this invention are liquids or waxes having a melting point of less than about 100° C. It is surprising that although such compounds are liquids or low melting waxes and are not soluble in the spinning dope, they can be heterogeneously dispersed in the dope and very little if any loss will occur during wet spinning, washing and other processing of the resulting fibers. As indicated by the formula, the number of halogen atoms will vary from one compound to another but the total number of aromatically bound chlorine or bromine atoms in the compound should be at least two and preferably at least three with not more than five per aromatic ring. Any compound having one of the formulae set forth above may be used such as, for example, di(2,4,6-tribromophenyl)adipate, di(2,4,6-tribromophenyl) sebacate, di(4-octanoyl dibromophenyl) propane, 4-nonyl, 2,6-dibromophenyl acetate, pentabromophenyl oleate, tribromophenyl stearate, pentabromophenyl stearate, di-(2,4,6-trichlorophenyl) sebacate, di(4-octanoyl dichlorophenyl) propane, trichlorophenyl stearate, di(2,4,6-trichlorophenyl) malonate, di(4 - bromopropoxy - 2,3,5,6-tetrabromophenyl) propane and the like. It is pointed out that compounds containing both aliphatically and aromatically bound halogen atoms can be used but such a compound must contain at least two aromatically bound halogen atoms.

The amount of halogenated aromatic compound included in the saline solution of the acrylonitrile polymer will vary with the percentage halogen in the compound and to some extent upon the particular halogen present. Any amount of brominated or chlorinated aromatic compound having the above formula will improve the flame resistance of an acrylonitrile polymer so all suitable concentrations in the spinning solution are broadly contemplated. Best results have been obtained so far with from about 1 percent to about 15 percent bromine or from about 2 percent to about 30 percent chlorine, or equivalent mixtures of bromine and chlorine based on the weight of acrylonitrile fiber in the spinning solution so it is preferred to use an amount within these ranges. With most halogenated aromatic compounds found suitable in accordance with this invention, the required amount of bromine and/or chlorine is supplied by from about 1 percent to about 20 percent by weight of the halogenated aromatic compound. The halogenated aromatic compounds may be used alone or in combination with other flame retardants such as antimony oxide and phosphorus compounds.

In practicing the invention, the halogenated aromatic compound is mixed sufficiently uniformly with a saline spinning solution and the resulting mixture is wet spun by conventional methods. To improve the flame resistance of a fiber spun from a saline solution, a spinning solution containing an acrylonitrile polymer, water and a saline solvent for the polymer such as sodium thiocyanate, zinc chloride or the like is stirred with the halogenated aromatic compound in a mixer adapted to impart a shearing action to the mixture until a substantially uniform dispersion of droplets of the halogenated compound in the spinning solution is obtained. The resulting mixture is then spun into an aqueous coagulating bath, stretched and dyed. The particles or droplets of liquid halogenated aromatic compound dispersed in the fiber are predominantly less than about 20 microns in cross-section.

The invention contemplates improving the flame resistance of any acrylonitrile polymer including those disclosed in U.S. 3,028,371. The term "acrylonitrile polymer" is used herein to mean acrylonitrile homopolymers and copolymers containing at least about 70 percent by weight acrylonitrile copolymerized with other mono-olefinic compounds of the type disclosed in U.S. 3,028,371 and other prior publications.

Although the invention is described herein to a large extent with respect to the production of fibers having improved flame resistance for convenience, it is also applicable to the production of other shaped articles such as tubes, films and the like.

As indicated by the formula of the halogenated aromatic compounds found advantageous for improving the flame resistance of acrylonitrile polymers, the halogen atoms must be aromatically bound and the sum of the carbon atoms in R_1 and R_2 of Formulae 1 and 2 must be greater than 9. The halogenated aromatic compounds are more resistant to chemical attack by aqueous saline solutions than halogenated aliphatic compounds. Such compounds are also retained to a greater extent by the shaped acrylonitrile polymer than are halogenated aliphatic compounds. Maximum retention is important not only for optimum flame proofing but also because the presence of halogen compounds in the solvent interferes with solvent recovery and introduces corrosion problems.

Any suitable saline solvent may be used to prepare the spinning solution such as, for example, those disclosed in Rein U.S. 2,140,921 and Cresswell 2,558,730. Specific examples of suitable salts are sodium thiocyanate, zinc chloride and the like. The amount of acrylonitrile polymer dissolved in the aqueous solvent can vary depending upon the composition of the polymer, its molecular weight and the particular salt used. Generally, from about 10 percent to about 20 percent by weight of the spinning solution will be polymer although even greater percentages can be used. The solutions containing more than 20 percent polymer may be spun into air prior to washing with water to remove the salt. The spinning solution may contain, in addition to the flame retardant, other additives or modifying agents, if desired. Conventional spinning equipment used for making filaments and fibers may be used.

The acrylonitrile polymers provided by this invention can be used to advantage in making draperies, carpets and other household furnishings.

In the following examples all parts are by weight unless otherwise specified.

EXAMPLE I

About 8 parts of 4-nonyl-2,6-dibromophenyl acetate are mixed with about 1000 parts of a spinning solution containing about 112 parts of an acrylonitrile copolymer, about 365 parts sodium thiocyanate and about 523 parts water and the mixture is agitated with a mixer adapted to impart a shearing action thereto until a substantially uniform dispersion of the bromine substituted compound in the spinning solution is obtained. The copolymer is about 10.7 percent methyl-methacrylate and about 89.3 percent acrylonitrile. The resulting mixture is wet spun from a wet-spinning apparatus into a coagulating bath containing about 10 percent sodium thiocyanate and about 90 percent water at about 0° C. A spinnerette of the type disclosed by Cresswell in U.S. 2,558,730 may be used.

The acrylic fiber thus produced contains the 4-nonyl-2,6-dibromophenyl acetate as small particulate inclusions. The fiber is completely lustrous and is self-extinguishing. From about 92 percent to about 96 percent or more of the 4-nonyl-2,6-dibromophenyl acetate added to the spinning solution is retained in the coagulated fiber and very little, if any, is lost as the fiber is dyed in water at 100° C. for about one hour.

EXAMPLE II

Example I is repeated except about 4.1 percent (based on the weight of copolymer) of di(2,4,6-tribromophenyl) sebacate are substituted for the 4-nonyl-2,6-dibromophenyl acetate. About 99 percent of the di(2,4,6-tribromophenyl) sebacate is retained in the fiber after spinning and about 92.5 percent thereof is retained after dyeing the fiber.

When about 6 percent di(2,3-dibromopropyl) sebacate are substituted for the di(2,4,6-tribromophenyl) sebacate,

only about 66.5 percent remains in the fiber after spinning and only about 12.7 percent remains after dyeing.

Substitution of about 4.3 percent tris(2,3-dibromopropyl) phosphate for the di(2,4,6-tribromophenyl) sebacate of this Example II results in the production of a fiber which retains only 89.5 percent of the phosphate after spinning and 39 percent after dyeing.

A fiber is obtained which retains only 88 percent of the halogen compound after spinning and 64 percent after dyeing when about 7 percent of a brominated fatty acid ester sold under the trademark Brominex are substituted for the di(2,4,6-tribromophenyl) sebacate of this Example II.

When about 11.8 percent of a chlorinated paraffin sold commercially as Hooker C1–40 are substituted for the di(2,4,6-tribromophenyl) sebacate the resulting fiber retains about 86 percent thereof after spinning and 73 percent after dyeing.

EXAMPLE III

Example I is repeated to prepare a series of fibers A through G except the halogen compound listed in the following Table I in the amount indicated is substituted for the 4-nonyl-2,6-dibromophenyl acetate.

TABLE I

	Flame retardant	Number carbon atoms in— R_1	Number carbon atoms in— R_2	Percent based on weight of copolymer	Percent retained After spin	Percent retained After dyeing
A	4-octyl 2,6-dibromophenol	8	0	5.7	71.5	54.0
B	4-nonyl 2,6-dibromophenol	9	0	6.2	79.5	69.5
C	4-tertiary butyl 2,6-dibromophenyl acetate	4	1	5.45	37.0	19.2
D	4-nonyl 2,6-dibromophenyl acetate	9	1	6.6	96.0	95.3
E	Tribromophenyl stearate	0	17	6.0	100.0	100.0
F	Pentabromophenyl stearate	0	17	5.1	96.0	96.0
G	Pentabromophenyl oleate	0	17	4.8	99.0	91.0

It is to be noted that the total number of carbon atoms in R_1 and R_2 of the flame retardant compound used in preparing fibers A through C is 9 or less and that the retention of the compounds by the fibers both after spinning and after dyeing is substantially less than the retention of the compounds by the fibers D through G. R_2 of the flame retardant compound used in preparing fibers D through G contains more than 9 carbon atoms.

EXAMPLE IV

Example I is repeated except about 8.4 parts of 4-nonyl, 2,6-dibromophenyl acetate and about 0.6 part of antimony trioxide are mixed with the 1000 parts spinning solution. The resulting fiber is self-extinguishing.

EXAMPLE V

Example I is repeated except a solution of about 2 parts of trioctylphosphate and about 7 parts of 4-nonyl 2,6-dibromophenyl acetate is dispersed in the spinning solution instead of the flame retardant of Example I. The fiber is self-extinguishing.

EXAMPLE VI

Example I is repeated except about 7 parts of di(4-octanoyltetrabromophenyl) propane are substituted for the 4-nonyl, 2,6-dibromophenyl acetate. About 100 percent of the di(4-octanoyltetrabromophenyl) propane is retained by the filament after spinning and about 99 percent thereof remains in the fiber after drying.

EXAMPLE VII

An intimate mixture is prepared containing about 50 parts di(4-bromopropoxy-2,3,5,6 tetrabromophenyl) propane, about 4 parts antimony oxide, about 22.5 parts of the copolymer of Example I, about 82 parts sodium thiocyanate and about 95.5 parts water. About 50 parts of the resulting mixture are substituted for the 4-nonyl, 2,6-dibromophenyl sebacate in the 1000 parts spinning solution of Example I and a fiber is prepared by the process of Example I. The fiber thus obtained contains about 2.6 percent bromine and about 0.25 percent antimony after drying. After mock dyeing, the fiber contains about 2.54 percent bromine and about 0.25 percent antimony. The fiber is self-extinguishsing.

Microscopic cross-sectional examination of the fibers produced by each of the foregoing examples shows that the fire retardant compound is present as minute droplets of liquid. Ordinarily, one would expect this liquid to be easily extracted from the fibers just as it proved to be with fibers A through C of Example III and those fibers produced by Example II using halogenated compounds not within the scope of this invention. However, when those compounds falling within the invention are used an insignificant amount of the fire retardant is, for some reason not yet explainable, extracted.

Although the invention has been described in detail for the purpose of illustration, it is to be understood that such detail is solely for that purpose and those skilled in the art can make changes therein without departing from the spirit and scope of the invention except that it is limited by the claims.

What is claimed is:

1. A solid shaped acrylonitrile polymer product prepared from a saline solution of polymer and having improved flame resistance containing an amount sufficient to impart flame resistance of a halogenated aromatic compound having a melting point below about 100° C. and having the formula

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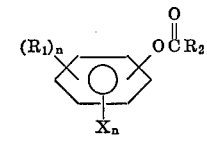

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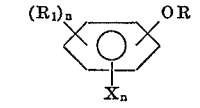

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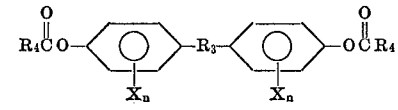

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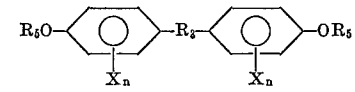

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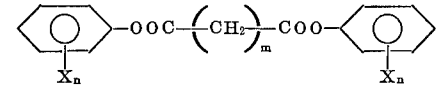


wherein R_1 is hydrogen, chlorine, bromine or an alkyl radical having from 1 to 9 carbon atoms; R_2 is a alkyl radical having 1 to 22 carbon atoms and the sum of the carbon atoms of R_1 and R_2 is greater than 9; R_3 is methylene, isopropylidene, oxygen or sulfur; R_4 is an alkyl radical containing at least one carbon atom; R_5 is a 2,3-dibromopropyl group; X is bromine or chlorine; m is an inter of from 0 to 22 and n is an integer of from 0 to 4

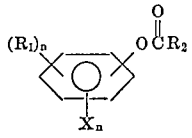
with the proviso that each formula contains at least two aromatically bound halogen atoms.

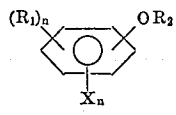
2. The product of claim 1 wherein the halogenated aromatic compound is 4-nonyl-2,6-dibromophenyl acetate.

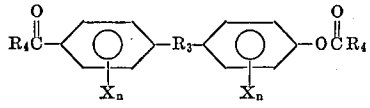
3. The product of claim 1 wherein said polymer contains from about 1 percent to about 20 percent of said halogenated aromatic compound.

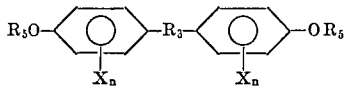
4. The product of claim 1 wherein said halogenated aromatic compound is di(4-octanoyl dibromophenyl propane, di(2,4,6-tribromophenyl) sebacate, pentabromophenyl oleate, tribromophenyl stearate, pentabromophenyl stearate or nonyldibromophenyl sebacate.

5. In the process for preparing the solid shaped acrylonitrile polymer product of claim 1 wherein the acrylonitrile polymer dissolved in saline solution is mixed with a flame-resisting agent and spun into a shaped article, the improvement which comprises using as the flame-resisting agent an effective amount of a halogenated aromatic compound having a melting point below about 100° C. and having the formula

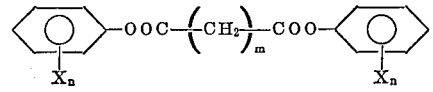
(1) 

(2) 

(3) 

(4) 

or

(5) 

wherein R_1 is hydrogen, chlorine, bromine or an alkyl radical having from 1 to 9 carbon atoms; R_2 is an alkyl radical having 1 to 22 carbon atoms and the sum of the carbon atoms of R_1 and R_2 is greater than 9; R_3 is methylene, isopropylidene, oxygen or sulfur; R_4 is an alkyl radical containing at least one carbon atom; R_5 is a 2,3-dibromopropyl group; X is bromine or chlorine; *m* is an integer of from 0 to 22 and *n* is an integer of from 0 to 4 with the proviso that each formula contains at least two aromatically bound halogen atoms.

6. The process of claim 5 wherein from about 1 percent to about 20 percent of said halogenated aromatic compound is mixed with said spinning solution.

7. The process of claim 5 wherein said spinning solution is an aqueous saline solution of an acrylonitrile polymer.

8. An acrylonitrile fiber prepared by spinning the composition of claim 1.

References Cited

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HAROLD D. ANDERSON, Primary Examiner

U.S. Cl. X.R.

260—29.6 AN, 45.95; 264—182 Dig 84

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,660,351 Dated May 2, 1972

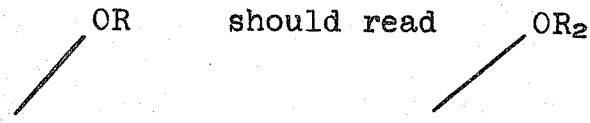
Inventor(s) Richard Frederick Schmidt & Joseph Jacinto Pellon

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

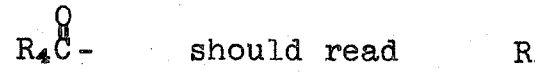
Col. 2, line 9, "resistance" should read -- resistant --.

Col. 3, line 2, "halogenated compound" should read -- halogenated aromatic compound --.

Col. 6, Claim 1, formula No. 2, right top side:



Col. 7, Claim 5, Formula No. 3, On the left side:



Signed and sealed this 19th day of September 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334