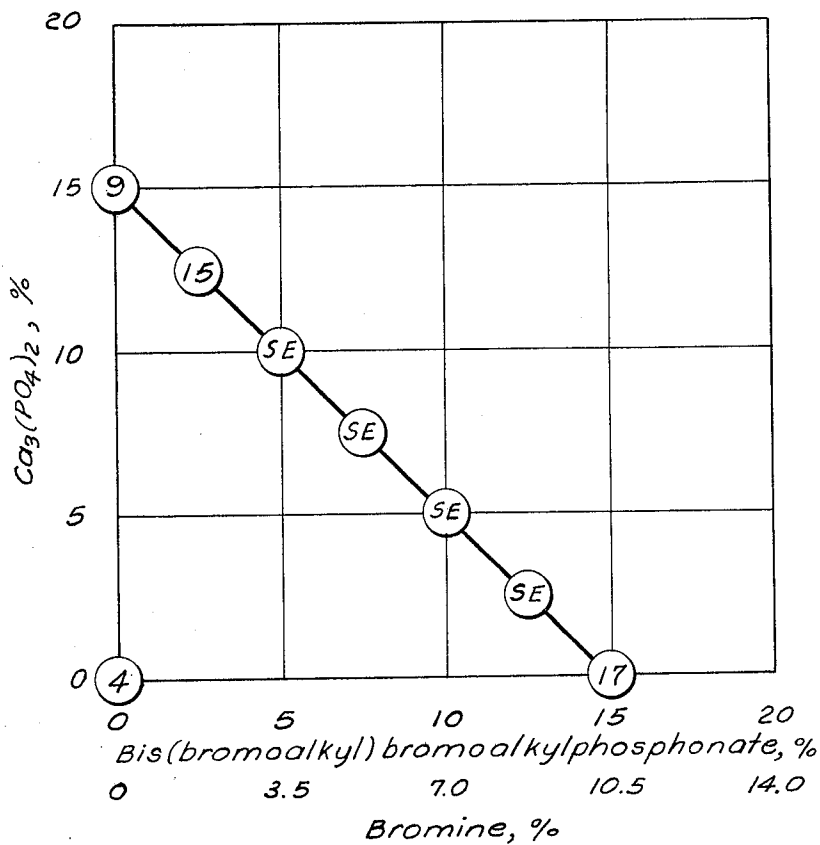


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FLAME-RESISTANT ACRYLONITRILE POLYMER COMPOSITION CONTAINING
A BROMINATED PHOSPHONATE AND CALCIUM PHOSPHATE
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FLAME-RESISTANT ACRYLONITRILE POLYMER COMPOSITION CONTAINING A BROMINATED PHOSPHONATE AND CALCIUM PHOSPHATE

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9 Claims. (Cl. 260—29.6)

This invention relates to compositions of matter that are especially adapted for use in spinning acrylonitrile polymer synthetic textile fibers or the like structures. It relates more particularly to spinnable solutions of such polymers in concentrated aqueous salt solutions having certain bis(bromoalkyl) bromoalkylphosphonates and substantially water-insoluble calcium phosphates dispersed therein. The invention is also concerned with shaped articles, especially filamentary structures having durable flame-resistant properties and, to methods for preparation of such compositions and articles.

The expression "flame-resistant" as employed herein, means a material which imparts resistance to afterflame after being ignited in an open flame and then removed from the flame.

The expressions "flameproofing mixture" and "flameproofing finish," as employed herein, mean a mixture or finish which imparts resistance to afterflame of a material which has been ignited in an open flame and then removed from the flame.

The expressions "self-extinguishing" and "flameproof," as employed herein, mean incapable of sustaining a flame until completely burned after a material has been ignited and then removed from the source of ignition.

Polyacrylonitrile and many of the fiber and film-forming copolymers of acrylonitrile may advantageously be fabricated by a wet spinning process wherein the polymer composition is extruded from compositions of the polymer in polyacrylonitrile-dissolving aqueous saline solvents, particularly aqueous solutions of zinc chloride and its saline equivalents. Such a procedure, as is well known in the art, is oftentimes referred to as salt-spinning with the fibers (or other shaped articles) obtained thereby being salt-spun. In salt-spinning, the fiber-forming aqueous saline spinning solution or other composition of the polymer is extruded during the spinning operation into a non-polymer-dissolving coagulation liquid, or spin bath, which frequently is a solution of the same salt or salts as are in the spinning solution.

Acrylonitrile polymers (including fiber-forming copolymers) particularly polyacrylonitrile, that are salt-spun in the referred-to manner are generally formed initially as aquagel intermediates. Such intermediates have a water-swollen or hydrated structure prior to their being finally irreversibly dried to the desired, characteristically hydrophobic, product. Advantageously, the aquagel structure of polyacrylonitrile and other fiber and film forming acrylonitrile polymers may be derived by the extrusion into and coagulation in an aqueous coagulating spin bath of a solution of the acrylonitrile polymer that is dissolved in an aqueous zinc chloride saline solvent therefor. It is usually desirable for zinc chloride to be at least the principal (if not the entire) saline solute in the aqueous saline solvent solution. If preferred, however, various of the saline equivalents for zinc chloride may also be employed in the aqueous saline solvent medium for the spinning solution and the coagulating bath utilized. These zinc chloride equivalents, as is well known, include various of the thiocyanates (such as calcium thiocyanate), lithium bromide and the salts and salt mixtures that are "solvent" members of the so-called "lyotropic" series as are disclosed, among other places, in U.S. 2,140,921; 2,425,192;

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2,648,592; 2,648,593; 2,648,646; 2,648,648; and 2,648,649.

Fabricated acrylonitrile polymer films, textile fibers and like filamentous articles derived from salt-spinning processes may be generically described as being capable of lying substantially in a single plane, having at least one major dimension, and at least one minor dimension less than about 0.1 inch, said articles being characterized by having orientation of the molecules parallel to one another and to a major surface of the article.

Articles produced from acrylonitrile polymers by the wet spinning process have excellent physical properties but suffer from one serious effect, namely, low resistance to afterflame when ignited in an open flame and then removed from the flame.

The flameproofing of flammable materials, such as textile and other fabric materials by application of flameproofing finishes and like treatments is not new. It is known, for example, that certain organic halides alone or in combination with certain organic and inorganic flameproofing substances often exhibit a flameproofing action. It remains an unpredictable problem however to discover such a compound, or compounds, which may satisfactorily be used to flameproof a given combustible organic material.

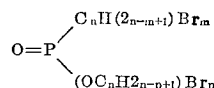
Accordingly, it is the primary object of the present invention to provide compositions of matter especially adapted for use in spinning synthetic films and textile fibers or like structures comprising solutions of high acrylonitrile polymers (i.e., those containing at least 85 weight percent of polymerized acrylonitrile in the polymer molecule).

A further object is to provide shaped articles from the compositions of the invention which have increased flame-resistance.

A still further object is to provide a method of producing the compositions and articles of the present invention.

Other and related objects will become evident from the following specification and claims.

In accordance with the present invention, high acrylonitrile polymer films and textile fibers (and shaped articles fabricated therefrom) having unexpectedly enhanced flame-resistance are produced from a polymeric spinning dispersion comprising (1) a fiber-forming acrylonitrile polymer, which polymer contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomeric material that is copolymerizable with acrylonitrile, (2) an aqueous saline solvent for polyacrylonitrile, said solvent having additionally dispersed therein (3) relatively small but effective amounts of a flameproofing mixture consisting essentially of (a) one or more bis(bromoalkyl)bromoalkylphosphonates having the general formula:



wherein n is a whole number from 2 to 4, m is a whole number from 1 to 2 and p is a whole number from 2 to 4 and, (b) a substantially water-insoluble calcium phosphate; wherein the phosphonate is present in amount sufficient to provide at least about 3 weight percent bromine, based on the weight of the flameproofing mixture; the calcium phosphate is present in amount of at least about 2.5 weight percent, based on the weight of the flameproofing mixture; and wherein the ratio of bromine to calcium phosphate is from about 1:3 and 4:1, based on the weight of bromine and calcium phosphate.

The acrylonitrile polymer employed in practice of the present invention is advantageously, polyacrylonitrile, although, as is readily apparent, any of the well-known

fiber and film-forming copolymers thereof that contain, polymerized in the polymer molecule, at least 85 weight percent of acrylonitrile with at least one other ethylenically unsaturated monomer that is copolymerizable with acrylonitrile may, generally, be utilized.

The acrylonitrile polymer employed is soluble in an aqueous saline solvent for acrylonitrile which, usually, has therein at least about 50-60 weight percent of zinc chloride or its saline equivalents. U.S. 2,776,946, among many other reference sources, sets forth many of the monomers which may be copolymerized or interpolymerized with acrylonitrile to produce binary or ternary acrylonitrile copolymers that are useful in the practice of this invention.

The bis(bromoalkyl)bromoalkylphosphonates to be employed in the flame-proofing mixture of the present invention are readily prepared by reacting an alkylene oxide containing from 2 to 4 carbon atoms in the molecule such as ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide or epibromohydrin, with phosphorous tribromide in a solvent such as o-dichlorobenzene, toluene, xylene or the like and thereafter raising the temperature of the reaction mixture to 150° C. or higher to cause rearrangement of the resulting phosphite to a phosphonate. The so-formed phosphonates may then be separated from the solvent and employed directly for incorporation into the herein defined polymeric spinning dispersion.

It is essential that the phosphonate be employed in combination with the water-insoluble calcium phosphate in the stated amounts to provide the optimum synergistic results of the invention. For example, flame-proofing mixtures of the type described by the present invention, but having the defined phosphonate ingredient present in amounts incapable of providing at least about 3 weight percent of bromine and/or mixtures containing less than about 2.5 weight percent of the defined calcium phosphate and mixtures wherein the ratio of bromine to calcium phosphate is other than from about 1:3 and 4:1 do not provide the desired results and are generally not useful for the purposes of the present invention.

The defined flame-proofing mixtures may be employed in any desired amount, depending on the degree of flame-proofing desired, up to the limit of its compatibility with the aqueous saline solution and/or the polymeric material dispersed therein. The maximum limit, however, is generally about 20 weight percent, based on the weight of the fiber-forming acrylonitrile polymer employed in the polymeric spinning dispersion. The amount of flame-proofing mixture present in shaped articles produced from salt-spun acrylonitrile polymers is dependent upon, and approximately in the same ratio as, the amounts of said mixture incorporated in the spinning solution.

It has further been found that the flame-proofing mixture must be present in the polymer solution in a minimum amount of about 15 weight percent, based on the weight of the acrylonitrile polymer, for impartation of self-extinguishing properties to non-fabricated fiber or foil prepared from the defined polymeric spinning solution. It is to be emphasized, however, that the obtainment of self-extinguishing properties for shaped articles, such as carpets, and the like articles prepared by fabrication of such fibers and/or foils, generally require much lower concentrations of the defined flame-proofing mixture, i.e., concentrations of the flame-proofing mixture as low as 5 weight percent or less, based on the weight of the fiber-forming acrylonitrile polymer ingredient of the polymeric spinning dispersion.

The flame-proofing mixtures of the present invention may be suitably dispersed in the polymeric spinning solution by first intimately admixing the ingredients of such flameproofing mixture with about equal weight proportions of the herein described aqueous polymeric spinning solution to form a concentrate. It is oftentimes advantageous to incorporate about 2 weight percent based

on the weight of spinning solution component of said concentrate of a suitable surface agent; (e.g. Aerosol C-61, a cationic 70 percent active reaction product of ethylene oxide and octadecylamine, octadecylcarbonic acid, and octadecyl guanidine).

The resulting concentrate mixture is advantageously reduced to a particle size sufficient to allow at least about 95 percent of the mixture to pass through a 325 mesh screen, prior to addition, with stirring, to the remaining desired amounts of the aqueous polymeric spinning solution.

The flameproofing mixtures of the present invention are compatible with the acrylonitrile polymers defined herein when used in the prescribed amounts, and, are substantially water-insoluble. The above combination of desirable properties prevents excessive extraction of the flameproofing mixtures from the polymer while coagulating the polymer solution in an aqueous nonpolymer-dissolving saline medium, and during subsequent water washing of the resulting aquagel and shaped article produced therefrom.

Shaped articles produced from acrylonitrile polymers by the process of the present invention do not significantly lose their flame-resistant properties even after repeated laundering.

It will be appreciated by those skilled in the art that various other materials can be added to the compositions of the present invention. Such materials include, for example, plasticizers, lubricants, dyes and pigments.

The following example, wherein all parts and percentages are to be taken by weight, illustrates the present invention but is not to be construed as limiting its scope.

Example 1

In each of a series of experiments, separate charges of about 35 grams of a solution consisting of 10 percent polyacrylonitrile, 54 percent zinc chloride, and 36 percent water, all based on the total weight of the solution, were placed in each of a series of bottles.

Varying percentages of bis(1,2-dibromopropyl)1,2-dibromopropanephosphonate, and tricalcium phosphate were individually admixed with approximately equal weight proportions based on the combined weight of the individual flameproofing mixtures of an aqueous polyacrylonitrile spinning solution as described herein. To each of the individual mixtures was individually added from about 2 weight percent based on the weight of the aqueous polyacrylonitrile spinning solution component of the mixture, of Aerosol C-61 (a cationic surface active agent as described previously).

Each of the resulting concentrate mixtures was individually ground in a mortar until a homogenous mixture having a particle size sufficient to allow at least about 95 percent of said mixture to pass freely through a 325 mesh screen was obtained.

Each of the individual homogeneous mixtures was separately added with stirring to the individual charges of aqueous polyacrylonitrile spinning solution described herein, until a homogeneous dispersion was, in each case, obtained.

The resulting individual samples were allowed to stand overnight at normal room temperatures to permit bubbles of entrapped air to escape.

Films about 0.01 inch thick 3 inches long and 7/8 inch wide were cast from each of the resulting spinning solutions on "Pyrex" glass plates using a stainless steel drawbar. The resulting films were coagulated by holding the coated plates in a stream of water at ambient temperature.

Within 1 or 2 minutes after casting, the films were detached from the glass plates and were thoroughly water washed until free from zinc chloride.

The films prepared in this manner were aquagels which were each then oriented about 10 percent by stretching while immersed in an aqueous medium at a temperature of at least 65° C.

Each of the oriented films were dried overnight at normal room temperatures and reference marks placed along the length of the dried film at 1 inch intervals, the first of such reference marks being placed ¼ inch from one end of the film.

Each of the films was individually placed in a clamp with the length of said film horizontally disposed and the width of the film vertically disposed. Ignition of the film was accomplished by a paper match held in such a manner as to have the flame contact the edge of the film as nearly parallel as possible. The film was ignited ¼ inch from the first mark and the time in seconds recorded for 1 inch of said film to be consumed by the flame.

Film compositions and burning rates are presented in the following Table 1.

Table 1

Sample No.	Ca ₃ (PO ₄) ₂ , percent (based on the weight of polymer)	Bis(1,2-dibromopropyl)1,2-dibromopropane-phosphonate, percent (based on the weight of polymer)	¹ Bromine, percent (based on the weight of polymer)	Burning rate (seconds required to burn 1 inch of film)
For Comparison:				
1.....				4
2.....	15			9
3.....	12.5	2.5	1.75	15
4.....		15	10.5	17
This Invention:				
5.....	2.5	12.5	8.75	(²)
6.....	5	10	7	(²)
7.....	7.5	7.5	5.25	(²)
8.....	10	5	3.5	(²)

¹ Derived from indicated amounts of bis(1,2-dibromopropyl)1,2-dibromopropanephosphonate.

² Self-extinguishing.

The information contained in the above Table 1 is further illustrated graphically in the attached drawing.

It is apparent from the results of Example 1 that self-extinguishing films were obtained using about 15 weight percent based on acrylonitrile polymer weight of a flameproofing mixture comprised of (a) at least about 3 weight percent of bromine based on the weight of acrylonitrile polymer, said bromine derived from bis-dibromopropyl-dibromopropane phosphate and, (b) at least about 2.5 weight percent of tricalcium phosphate, the ratio of bromine to tricalcium phosphate being variable between about 1:3 and 4:1.

It is further apparent from the results of Example 1 that there is a synergistic effect as regards flame-resistance between the tricalcium phosphate and the indicated phosphonate; in other words, the tricalcium phosphate co-acts with the phosphonate to produce a high degree of flame-resistance to salt-spun acrylonitrile polymers.

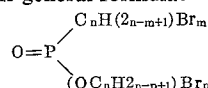
For purposes of comparison, it has been found that utilization of water-soluble salts of phosphoric acid such as tris(2-ethylhexylphosphate) as a replacement for the substantially water-insoluble calcium phosphate ingredient of the defined flame-proofing mixture does not provide the advantageous results of the present invention. Further, it has been found that the replacement of the bis(bromoalkyl) bromoalkylphosphate ingredient of the defined flameproofing mixture with amounts of a brominated salicylanilide sufficient to provide equivalent amounts of bromine, and comprising essentially equal parts by weight of the 3,4',5-tribromo isomer and the 4',5-dibromo isomer, also did not provide the beneficial results of the present invention.

Similar good results as illustrated herein are obtained, however, utilizing any of the defined fiber-forming acrylonitrile polymers and flameproofing mixtures in the manner prescribed by the present invention.

What is claimed is:

1. Composition comprising a spinnable dispersion of

(1) a fiber-forming acrylonitrile polymer which contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomer that is copolymerizable with acrylonitrile (2) an aqueous saline solvent for polyacrylonitrile, said solvent having additionally dispersed therein (3) up to about 20 weight percent, based on the weight of the fiber-forming polymer, of a flameproofing mixture consisting essentially of (a) a bromine-containing phosphonate having the general formula:



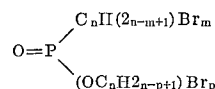
wherein n is a whole number from 2 to 4, m is a whole number from 1 to 2 and p is a whole number from 2 to 4,

and (b) a substantially water-insoluble calcium phosphate; wherein said bromine-containing phosphonate is present in amount sufficient to provide at least about 3 weight percent bromine, based on the weight of said flameproofing mixture; wherein said calcium phosphate is present in amount of at least about 2.5 weight percent based on the weight of the flameproofing mixture; and wherein the ratio of bromine to calcium phosphate is from about 1:3 and 4:1.

2. The composition of claim 1 wherein said fiber-forming acrylonitrile polymer is polyacrylonitrile.

3. The composition of claim 2 wherein said bromine-containing phosphonate is bis(1,2-dibromopropyl)1,2-dibromopropanephosphonate and said substantially water-insoluble phosphate is tricalcium phosphate.

4. In the process of producing articles from a spinning solution of a fiber-forming acrylonitrile polymer which contains in the polymer molecule at least about 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomer which is copolymerizable with acrylonitrile, which polymer is dissolved as a spinnable composition in an aqueous saline solvent for said fiber-forming polymer; the improvement consisting of dispersing in said spinning solution up to about 20 weight percent, based on the weight of the fiber-forming polymer of a flameproofing mixture consisting essentially of (a) a bromine-containing phosphonate having the general formula:



wherein n is a whole number from 2 to 4, m is a whole number from 1 to 2 and p is a whole number from 2 to 4, and (b) a substantially water-insoluble calcium phosphate; wherein said bromine-containing phosphonate is present in amount sufficient to provide at least about 3 weight percent bromine based on the weight of said flame-

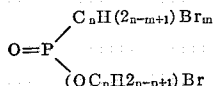
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proofing mixture; wherein said calcium phosphate is present in amount of at least about 2.5 weight percent based on the weight of the flameproofing mixture; and wherein the ratio of bromine to calcium phosphate is from about 1:3 and 4:1.

5. The process of claim 4 wherein said fiber-forming acrylonitrile polymer is polyacrylonitrile.

6. The process of claim 5 wherein said bromine-containing phosphonate is bis(1,2-dibromopropyl)1,2-dibromopropanephosphonate and said substantially water-insoluble calcium phosphate is tricalcium phosphate.

7. A flame resistant article of manufacture capable of lying substantially in a single plane having at least one major dimension and at least one minor dimension less than about 0.1 inch, comprised of (1) a fiber-forming acrylonitrile polymer which contains in the polymer molecule at least 85 weight percent of acrylonitrile, any balance being another monoethylenically unsaturated monomer that is copolymerizable with acrylonitrile and (2) uniformly dispersed therethrough up to about 20 weight percent, based on the weight of the fiber-forming polymer, of a flame proofing mixture consisting essentially of (a) a bromine-containing phosphonate having the general formula:



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wherein n is a whole number from 2 to 4, m is a whole number from 1 to 2 and p is a whole number from 2 to 4, and (b) a substantially water-insoluble calcium phosphate; wherein said bromine-containing phosphonate is present in amount sufficient to provide at least about 3 weight percent bromine, based on the weight of said flameproofing mixture; wherein said calcium phosphate is present in amount of at least about 2.5 weight percent, based on the weight of the flameproofing mixture; and wherein the ratio of bromine to calcium phosphate is from about 1:3 and 4:1.

8. The article of claim 7 wherein said fiber-forming acrylonitrile polymer is polyacrylonitrile.

9. The article of claim 8 wherein said bromine-containing phosphonate is bis(1,2-dibromopropyl)1,2-dibromopropanephosphonate and substantially water-insoluble calcium phosphate is tricalcium phosphate.

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