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PRODUCTION OF FLAME-RETARDANT SPUN-FORMED MATERIAL

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4 Claims

ABSTRACT OF THE DISCLOSURE

Spun-formed material such as spun-bonded polyester non-woven fabric is rendered flame retardant or self-extinguishing by treatment with an aqueous solution of a water soluble polyhaloalkyl ester of phosphoric acid in which the halogen is bromine or chlorine, and in which the alkyl radical contains two through six carbon atoms; for example, the ammonium salt of bis (2,3-di-bromopropyl) phosphate. If the phosphate ester is not sufficiently water soluble and does not readily form water soluble salts, an aqueous emulsion can be used; for example, an oil in water emulsion of tris (2,3-dibromopropyl) phosphate.

The present invention relates to an improved method for treating spun-bonded or spun-formed thermoplastic materials to render them flame retardant or self-extinguishing and to the materials produced thereby.

Spun-bonded materials are normally produced by an integrated process of spinning and bonding thermoplastic filaments. Whereas conventional non-woven materials including those produced from thermoplastic materials, are composed of short fibers joined together with a suitable binder or adhesive spun-bonded thermoplastic materials are usually made up of randomly arranged continuous filaments bonded at the crossover points. Such filaments may be subjected to heat and pressure during a rolling operation so that the fibers are criss-crossed at random and bonded to each other. The random nature of this spun-bonded non-woven material promotes uniformity of strength and elongation in all directions and has produced a material resistant to stress particularly tensile stress, as compared with other non-woven materials.

The filaments used for such spun-bonded material may be produced from what is known as melt-spun material; that is, the polymer or copolymer such as an appropriate polyolefin or polyester is melted in a suitable container. It is then extruded through an orifice at a relatively high pressure and at an elevated temperature. For example, it could be extruded through a die or nozzle but it is not extruded through a spinnerette in the conventional manner for forming synthetic fibers. As a result of this method of production, these melt-spun filaments are not fully crystallized and therefore do not possess complete orientation of the crystals in one direction so that they are not true crystallites and are not really fibers in the strict sense of that term. In fact, they possess inherent imperfections or crystallite deformations which are randomly disposed and which provide sites for the absorption of additives including flame retardant additives. Such sites are effective for such absorption without necessarily involving interstices or pores although some spun-bonded materials do possess such pores similar to those of conventional non-woven cellulosic materials. On the other hand, filaments suitable for the spun-bonded operation may be produced from a split film of the extruded material. Suitable knife edges as on a roller may be used to provide them, or the die or orifice may contain a multiplicity of needles or points to produce a punctured film type of material in-

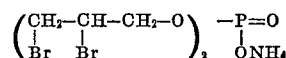
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stead of split film filaments. Such a punctured film possesses the same hybrid plastic and fibre characteristics as does the spun-bonded material. Also, the rollers, if used, may have other conformations, embossments or grooves to provide a filament or film having various shapes or configurations.

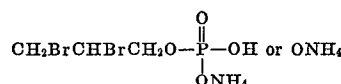
In some respects spun-bonded or spun-formed material resembles non-woven cellulosic material such as paper, and in other respects, it resembles a woven fabric because of the inherent characteristics of the material from which it was produced. For example, it possesses textile-like characteristics, has a soft hand, and may be washed without appreciable loss of these qualities. Consequently, spun-bonded or melt-spun materials can be put to various uses; but they have been found particularly desirable for the production of disposable apparel and other uses in connection with clothing such as garment interlining. They may, of course, find still other uses such as backing for rubber or plastic compositions. To date the spun-bonded materials of commerce have been made from polyesters or polypropylene; but other thermoplastic materials capable of being spun-bonded or melt-spun may be utilized, such for example as polyethylene or acrylic polymers. Due at least in part to the inherent nature of the material from which these spun-bonded or melt-spun materials are produced, and to the relatively open structure of some of them, these materials are quite flammable. Accordingly, it is important to impart flame retardant characteristics to them particularly in view of their use in apparel, fabrics and other materials commonly used by the public.

The present invention provides a method of treating such spun-bonded or melt-spun materials to render them fire-retardant and in some cases self-extinguishing without impairing their desirable physical characteristics. Generally speaking, it involves impregnating or similarly treating such material with a fire retardant comprising (a) an aqueous solution containing a water soluble mono or bis polyhaloalkyl ester of phosphoric acid or a water soluble salt thereof; or (b) an aqueous emulsion of such acids and salts, or of the corresponding tris compounds. The alkyl radical may be straight chained or branch chained and contains two through six carbon atoms. The halogens of the haloalkyl group may be either bromine, chlorine, or both. It should be noted, in particular, that the solution or emulsion is aqueous in character, thus avoiding the difficulties and hazards attendant upon the use of an alcohol or some other organic solvent.

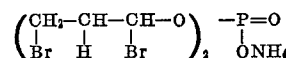
More particularly, in carrying out the present invention, the use of an aqueous solution of the ammonium salt of bis (2,3-dibromopropyl) phosphoric acid is especially recommended.



Instead of this compound, the ammonium or di ammonium salt of the mono acid may be used,



or the ammonium salt of the isopropyl analogue may be used; that is, bis (1,3-dibromoisopropyl) phosphate.



The ammonium salt of the mono acid corresponding to this isopropyl analogue may be used also.

It is necessary for present purposes that these fire retardant compounds be water soluble or that a satisfactory

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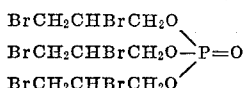
aqueous emulsion be provided. The tris compounds corresponding to the mono and bis compound mentioned above are not water soluble and neither are the bis acids themselves. At least these compounds are not sufficiently water soluble to be practical for forming effective aqueous solutions. Water soluble salts of these compounds may be used if a solution is utilized, but the ammonium salts, although particularly recommended, are not the only ones which could be so employed. Any suitable water soluble salt of these acids could be used. For example, those formed from sodium, magnesium and various amines especially the so-called simple amines, such as pyridine and butylamine could be employed. The corresponding salts of the mono acids could also be employed, if desired, although the mono acids, since they contain the polarizing



group, are sufficiently water soluble to be used as the acid.

An aqueous emulsion would normally be used only if it proved to be impossible or impracticable to obtain an aqueous solution for the particular fire retardant material being utilized. However, an emulsion could be produced using a fire retardant which is considered water soluble or at least could be so considered under some conditions. For instance, an oil-in-water emulsion might be formed employing relatively large quantities of a suitable organic or petroleum solvent which is a solvent for the fire retardant but is substantially immiscible in water. But solutions are recommended over emulsions.

If the fire retardant contemplated is not water soluble or is not sufficiently water soluble to form an effective solution, an emulsion is, of course, utilized. Such fire retardants include the tris acids such as tris (2,3-dibromopropyl) phosphate



Also, the bis acids themselves as contrasted with their water soluble salts are not sufficiently soluble for present purposes such for instance as bis (2,3-dibromopropyl) phosphate. Since the bis acids have an acid group available for reaction, it is not too difficult to form a water soluble salt such as the ammonium salt referred to above. The tris acids have no such acid group available and therefore it is very difficult to form water soluble salts. In fact, as a practical matter, it is too difficult and expensive to be satisfactory. Some amine salts might be used, but emulsions of these acids are preferable. The mono acid is sufficiently water soluble to be used in solution, if desired, although its water soluble salts could also be used of course. Chlorine may be substituted for one or more of the bromines in the fire retardant compounds mentioned above in one of their alkyl chains or in two or three of them in the case of the bis or tris compounds. And the alkyl chain or chains may contain from two through six carbon atoms, either straight or branch chained with two bromines or two chlorines, or one bromine and one chlorine substituted in one or more of the chains.

Some other fire retardants of the present invention adapted to provide an aqueous solution include the ammonium salt of bis (1-bromo-3-chloroisopropyl) phosphoric acid, bis (2-bromoethyl) phosphoric acid, bis (1,3-dibromoisopropyl) phosphoric acid, a mixture of bis (2,3-dibromopropyl) phosphoric acid and bis (1-bromo-3-chloroisopropyl) phosphoric acid, a mixture of bis (2,3-dibromopropyl) phosphoric acid and bis (2-bromoethyl) phosphoric acid, a mixture of bis (1,3-dibromoisopropyl) phosphoric acid and bis (2 3-dibromopropyl) phosphoric acid, a mixture of bis (1,3-dibromoisopropyl) phosphoric acid and bis (2-bromoethyl) phosphoric acid, a mixture of bis (1-bromo-3-chloroisopropyl) phosphate and bis (2-

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bromoethyl) phosphoric acid, a mixture of bis (2,3-dibromopropyl) phosphoric acid and the mono (2,3-dibromopropyl) phosphoric acid, a mixture of bis (1-bromo-3-chloroisopropyl) phosphoric acid and 1-bromo-3-chloroisopropyl phosphoric acid, a mixture of bis (1,3-dibromoisopropyl) phosphoric acid and 1,3-dibromoisopropyl phosphoric acid, and a mixture of bis (2-bromoethyl) phosphoric acid and 2-bromoethyl phosphoric acid.

The fire retardant compounds of the present invention which are not water soluble are, unfortunately, also especially difficult to formulate into a satisfactory aqueous emulsion. While such emulsions may be formed initially with a number of emulsifying agents, such emulsions are not very stable. To be useful for present purposes, the emulsions should withstand shipment and processing conditions for the material being treated.

Accordingly, it is recommended for these fire retardant compounds that an emulsion-forming concentrate be first produced utilizing an organic solvent and a particular emulsifying agent, and that this concentrate be used with water in forming an oil in water type emulsion controlling the quantity of water so as to provide the desired concentration of the flame retardant compound. In this connection, the organic solvent should be substantially immiscible with water; it should have a specific gravity as low as possible; that is, approximate that of water and have a flash point high enough to avoid shipping restrictions (preferably higher than 80° F.). The emulsifying agent recommended is an oil soluble metal sulfonate blended with a polyoxymethylene ether. The emulsion is preferably produced by mixing the concentrate with water under agitation. The amount of the concentrate used may differ quite a bit and, in fact, may vary from about 10 to about 50% by weight of the emulsion. For details of these emulsions and their preparation, see co-pending application Serial #769,360 entitled "Production of Fire Retardant Emulsions," John H. Todd, which application has an assignee in common with the present application.

The solvents or emulsions of the present invention may be applied to the material being treated very easily in any appropriate manner while using conventional equipment. For example, spraying, dipping or padding methods and apparatus may be utilized. Suitable rollers may be used to remove excessive solution or emulsion depending upon the particular material being treated and the type of equipment which is available.

The following examples are presented by way of further illustration of the invention but should not be construed as limiting. All parts and percentages including those in the examples are by weight unless otherwise indicated.

EXAMPLE I

A piece of spun-bonded polyester known as "Reemay" (E. I. du Pont de Nemours Co., Wilmington, Del.) was immersed in an aqueous solution of the ammonia wash resulting from the neutralization of crude tris (2,3-dibromopropyl) phosphate. The tris (2,3-dibromopropyl) phosphate was produced by the reaction of 2,3-dibromopropanol and phosphorus oxychloride, and the ammonia wash is a by-product. It contained approximately 30% solids as received and is essentially a solution of the ammonium salt of bis (2,3-dibromopropyl) phosphate, but contained small amounts of mono- (2,3-dibromopropyl) phosphate and of ammonium chloride. This relatively crude solution was diluted 3 to 1 with water; that is, 100 grams of ammonium solution plus 300 ml. of water was used.

This particular specimen weighed 41.2 grams prior to treatment and was about 1 square yard in size. After immersion in the solution, it was wrung out to remove excess liquid and was then air dried. If preferred, it could be dried in an oven for about 10 minutes at about 140° C. The piece weighed 51.6 grams after drying; that is, the add-on on the dry basis was 25.2%. The dry add-on is the

increase in weight of the specimen after treatment and drying over its weight before treatment.

Several 1 inch by 12 inch strips were cut from the treated material and were suspended vertically from a suitable support. No ignition occurred when the specimen was contacted with a flame of a wooden match (Fire Resistance Match Method No. 30-27, Material Testing Laboratory, Fisher Body Division, General Motors Corporation, Engineering Section). This test is described in detail hereinafter. The non-treated material; that is, the control, was consumed. Also, the untreated strip ignited fluffed cotton placed immediately below each test strip. But the treated strip did not do so. This technique is used to determine whether or not the tested material will drip or melt and thus be a fire hazard even if it did not spread the flame front.

Instead of the ammonia wash mentioned above, a relatively pure solution of the ammonium salt of bis(2,3-dibromopropyl)phosphate could be used. It is recommended, however, that the solution be adjusted to produce a specific gravity of about 1.10 and at least a 20% solids content in order to produce the desired add-on.

A piece of spun-bonded polypropylene was also treated in the same manner as the spun-bonded polyester. It differed only in that the dry add-on was about 28%. A self-extinguishing material was produced according to the same match test; and the treated material did not ignite the fluffed cotton.

EXAMPLE II

A piece of spun-bonded polyester similar to that referred to in Example 1 was cut into several strips 3 inches by 12 inches in size. One of these strips was immersed in a solution of the ammonium wash referred to in Example 1. Since this material is a by-product, it varies from time to time when received as to its solids content. This particular material had a solids content of approximately 28.4% and a starting specific gravity of 1.123 (21° C.). This starting solution was diluted with water so as to produce a solids content of approximately 8.0% and a specific gravity of 1.060 (21° C.). This required a dilution of 100 ml. of water per 100 ml. of the solution as received.

After immersing, the specimen was air dried although it could have been dried in an oven as explained in Example 1. The specimen weighed 0.91 grams prior to treatment. The dry add-on was .22 grams; that is, 24.2%. After treatment, the specimen was cut into three 1 inch by 12 inch strips and tested by the Match Test referred to in Example 1. None of the strips ignited; that is, they were self-extinguishing by the test. Also, there were no drippings or melted portions sufficient to ignite a ball of fluffed cotton placed under the strips.

EXAMPLE III

A 12 inch by 12 inch square of "Reemay" spun-bonded polyester material was immersed in a solution of the ammonium salt of bis(2,3-dibromopropyl)phosphate having approximately a 25% solids content. This particular piece weighed 6.1 grams prior to treatment. After removal of excess solution and drying in the manner previously explained, it was determined that the dry add-on was 2.3 grams; that is, 60.5%.

This material was tested for fire retardant characteristics by the AATCC test and found to have a 3/4 inch char and no afterglow. According to this test, the material was self-extinguishing. The AATCC test is explained in detail hereinafter.

EXAMPLE IV

200 grams of tris(2,3-dibromopropyl)phosphate were dissolved in 150 grams of a petroleum solvent "LA-30." This solvent is produced by Leonard Refineries Inc., Alma, Mich. It has an API gravity of 29.7, a flash point of 112° F. (Tag Closed Cup Method ASTM), and it boils in the range of 316° to 330° F. 40 grams of an emulsifying agent

"Emcol H-141" (an emulsifier comprising an oil soluble calcium salt of a sulfonate blended with a polyoxyethylene ether—Witco Chemical Co., Inc., Organic Chemical Division, Chicago, Ill.) was then added to the solution and dissolved therein. The solution had a specific gravity of 1.296. 400 ml. of deionized water was placed in a Waring blender and 78 grams of the concentrate referred to immediately above was stirred into it while the blender was operated at a high speed. This stirring operation took about two minutes to form a stable aqueous emulsion.

A 3 inch by 12 inch piece of spun-bonded polyester fabric was dipped into this aqueous emulsion and after the dipping operation was squeezed to remove excess emulsion. It was then dried for 30 minutes at 130° C. The dry add-on was 0.28 gram. This piece was cut into three 1 inch by 12 inch pieces and tested by the test method referred to in Example 1. All 3 strips were self-extinguishing according to this test.

Test methods for evaluating the fire retardant characteristics of various materials such as fabrics, non-woven cellulosic materials, etc., are rather empirical. Tests tend to be devised for particular materials or uses, and data obtained from one test are especially difficult to correlate with that from another. And what is "fire-retardant" as contrasted with "non-burning" or "self-extinguishing" according to one test may not be so according to another, or a given test may be altogether unsuitable for some particular material. The "First Resistance Method No. 30-27" and the AATCC tests relied upon for present purposes are believed to be appropriate for the materials treated according to the present invention. Other tests might be used, of course, although some of them are more suitable for other materials. For example, ASTM test 1692-59T referred to below is intended primarily for plastics or plastic coated materials.

Fire-Resistance Match Method No. 30-27, Material Testing Laboratory, Fisher Body Division, General Motors Corporation, Engineering Section involves the following procedure: A specimen of the material, 1 inch by 12 inches, is cut. A gage mark is made in the middle of the 12 inch length for each specimen and the specimen is suspended vertically lengthwise from a clamp. A wooden match is lit and used to ignite the bottom of the 1 inch edge of the specimen. The specimen is exposed to the flame of the match until the match is consumed (about 15 seconds). If the flame is extinguished within 5 seconds after the match is consumed and the specimen is not burned past the center gage mark, the fabric is considered to be self-extinguishing. If any of the specimen are burned beyond the center gage mark, or if they produce afterglow for more than one minute after the fabric flame has gone out, the specimen may be considered as fire retardant; but not as self-extinguishing. By comparing each specimen with the others or with a control, one can obtain a measure of the first retardation of various treated fabrics as compared to each other, or as compared to untreated material.

In order to obtain results which can be duplicated or to obtain meaningful results if comparative data is sought for this or other test procedures, it is often necessary to precondition the specimen prior to the actual test procedure mentioned above. There are various accepted ways of preconditioning. Usually they involve preheating the specimen for a specified time and sometimes at a specified relative humidity. One accepted method of preconditioning is described in ASTM test 1692-59T, ASTM Standards 1967, Part 27, pages 556-559, published by the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa.

The AATCC test is intended in particular for use with industrial fabrics and was devised by the American Association of Textile Chemists and Colorists. According to this test, a specimen is mounted on a frame in a test chamber and is subjected to a standard flame under controlled conditions. The specimen is then evaluated for afterflam-

ing, afterglow and range of char. A cabinet is provided and the sample holder is arranged to securely hold the fabric along its two vertical edges. The specimen is held in a vertical position with respect to a Bunsen burner so that its lower edge will extend $\frac{3}{4}$ of an inch into the flame when the burner is ignited. The test is conducted after the sliding panel of the cabinet is closed by subjecting the specimen to the flame of the Bunsen burner for 12 seconds. The burner is then extinguished. The fabric may be considered fire retardant if afterflaming does not exceed 2 seconds, and the charring does not exceed certain specified limits. These limits differ with the weight per square yard of the fabric tested. AATCC Standard Test Method 34-1966, Technical Manual (1966) of the American Association of Textile Chemists and Colorists, B135 and 136, published for the Association by Howes Publishing Company, Inc., 44 E. 23rd Street, New York, N.Y.

What is claimed is:

1. A method of rendering a melt-spun polyester material fire-retardant which comprises treating said material with a solution consisting essentially of an aqueous medium containing as the fire-retarding agent a water soluble poly-halo alkyl mono- or bis- acid ester of phosphoric acid, a water soluble salt of said acid, or mixtures thereof, wherein the alkyl radical contains 2 to 6 carbon atoms and the halogen is either bromine or chlorine or both, and thereafter drying the melt-spun polyester material so treated.

2. A method according to claim 1 in which the dissolved solids content of the solution and the time of treatment are such that the dry add-on to the melt-spun polyester material is at least 20%.

3. A method according to claim 1 in which the solute of the aqueous solution consists of a water soluble salt of bis(2,3-dibromopropyl)phosphate.

4. A method according to claim 1 in which the aqueous solution contains at least a 20% solids content consisting essentially of the ammonium salt of bis(2,3-dibromopropyl)phosphate.

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