PATENT SPECIFICATION

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(54) FLAME-RETARDED, REINFORCED THERMOPLASTIC POLYESTER COMPOSITION HAVING IMPROVED ARC RESISTANCE AND PROCESS FOR PREPARING SAME

(71) We, GENERAL ELECTRIC COMPANY, a corporation organised and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to reinforced flame-retardant thermoplastic compositions having improved dielectric properties and a process for the preparation thereof. More particularly, it pertains to compositions comprising a linear high molecular weight polyester, an aromatic polycarbonate flame-retardant, a reinforcing agent and talc and a process for improving the arc track resistance of reinforced, flame-retardant linear high molecular weight polyester compositions without impairing the flame-retardancy and other desirable properties such as strength, modulus and heat deflection temperature.

High molecular weight linear polyesters and copolymers of glycols and terephthalic or isophthalic acid have been available for a number of years. These are described *inter alia* in Whinfield et al, U.S. 2,465,319 and in Pengilly, U.S. 3,047,539. These patents disclose that the polyesters are particularly advantageous as film and fiber-formers.

With the development of molecular weight control, use of nucleating agents and two-step molding cycles, poly(ethylene terephthalate) has become an important constituent of injection moldable compositions. Poly(1,4-butylene terephthalate), because of its very rapid crystallization from the melt, is uniquely useful as a component in such compositions. Workpieces molded from such polyester resins, in comparison with other thermoplastics, offer a high degree of surface hardness and abrasion resistance, high gloss, and lower surface friction.

A useful family of such compositions are those which are glass-reinforced, e.g., with from 10 to 40% of filamentous glass, based on the weight of glass and polyester component, and rendered flame-retardant by the incorporation of a flame-retarding amount of a flame-retarding component.

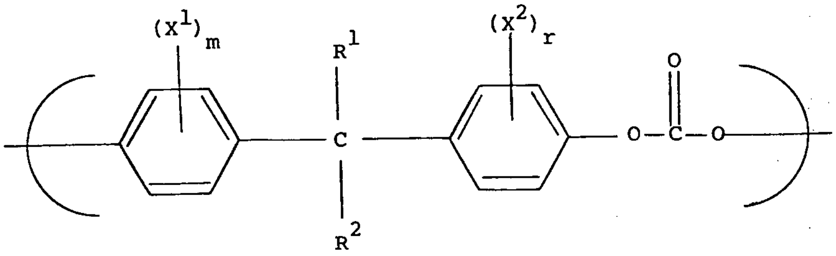
However, there is a need to improve the high voltage track rate of these compositions. For example, the high voltage track rate, as measured according to Underwriter's Laboratory Bulletin 494, of a 30% glass reinforced, non-flame-retardant poly(1,4-butylene terephthalate) composition is 0.60 to 0.87 inches per minute. The addition of a flame-retardant to this same 30% glass reinforced poly(1,4-butylene terephthalate) composition results in a track rate of 8.2 to 11.6 inches per minute. The higher rate indicates less desirable arc track resistance.

It has now been discovered that the incorporation of talc improves the high voltage arc track resistance of reinforced, flame-retarded polyester resins while not adversely affecting the flame-retardancy and the other excellent physical properties of the composition.

According to this invention, there are provided thermoplastic compositions with improved arc track resistance useful for molding, e.g., injection molding, compression molding, or transfer molding, comprising:

(a) a high molecular weight linear polyester resin;

(b) a flame-retarding amount of an aromatic carbonate homopolymer having repeating units of the formula:



wherein R^1 and R^2 are hydrogen, alkyl, or phenyl, X^1 and X^2 are bromine or chlorine and *m* and *r* are from 1 to 4; or an aromatic (copoly-) carbonate in which from 25 to 75 wt. percent of the repeating units comprise chlorine- or bromine-substituted dihydric phenol units and the remainder of the repeating units comprise dihydric phenol, glycol or dicarboxylic acid units or mixtures thereof;

(c) a reinforcing amount of a reinforcing agent; and

(d) talc in an amount sufficient to effect an appreciable increase in the arc track resistance of the composition.

In a further embodiment of the present invention a process is provided for increasing the arc track resistance of reinforced flame-retarded thermoplastic compositions, said process comprising admixing talc with a high molecular weight linear polyester resin, a flame-retardant as defined above and a reinforcing agent.

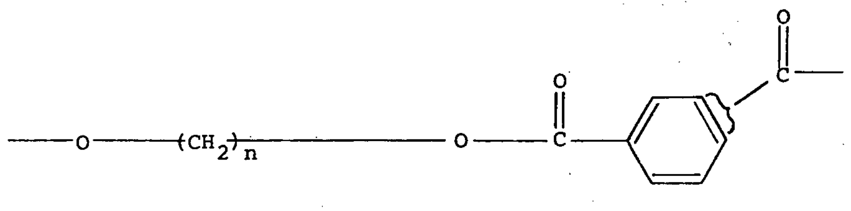
The talc filler, which is employed in the practice of the present invention is used in a finely divided form and the particle size may vary widely as, for instance, from 0.01 to 1,000 microns, with the preferred particle size being less than 50 microns. The particle may also assume any naturally existing or desired shape as, for instance, acicular, fibrous, or flat platelets.

The amount of talc filler added to the reinforced flame-retarded polyester composition is that amount which is sufficient to effect an appreciable increase in the arc track resistance of the composition, for instance, ratings of less than 2.5 inches per minute (UL Bulletin 494). In general, the concentration of talc required to effect an increase of this magnitude is from 10% to 50% by weight, based on the total composition. An amount of talc of from 10 to 30% by weight is preferred. In addition to increasing the arc-track resistance, these concentrations of talc also provide the polyester compositions with enhanced flame-retardancy.

The high molecular weight normally flammable linear polyesters used in the present invention are polymeric glycol esters of terephthalic acid and isophthalic acids. They are available commercially or can be prepared by known techniques such as by the alcoholysis of esters of the phthalic acid with a glycol and subsequent polymerization, by heating glycols with the free acids or with halide derivatives thereof, and similar processes. These are described in U.S. 2,465,319 and U.S. 3,047,539, and elsewhere.

Although the glycol portion of the polyester can contain from two to ten carbon atoms, it is preferred that it contain from two to four carbon atoms in the form of linear methylene chains.

Preferred polyesters will be of the family consisting of high molecular weight, polymeric glycol terephthalates or isophthalates having repeating units of the general formula



wherein *n* is a whole number of from two to four, and mixtures of such esters, including copolyesters of terephthalic and isophthalic acids of up to 30 mole % isophthalic units.

Especially preferred polyesters are poly(ethylene terephthalate) and poly(1,4-butylene terephthalate). Special mention is made of the latter because it crystallizes at such a good rate that it may be used for injection molding without the need for nucleating agents or long cycles, as is sometimes necessary with poly(ethylene terephthalate).

Illustratively, high molecular weight polyesters will have an intrinsic viscosity of at least 0.4 deciliters/gram and preferably, at least 0.7 deciliters/gram, as measured in a 60:40 phenol/tetrachloroethane mixture at 30°C. At intrinsic viscosities of at least 1.1 deciliters/gram, there is a further enhancement in toughness of the present compositions.

The reinforcing agents employed herein are well known but illustratively, they may be metals, such as aluminum, iron or nickel particles, or non-metals, such as carbon filaments, silicates, such as acicular calcium silicate, asbestos, titanium dioxide, potassium titanate and titanate whiskers, wollastonite, glass flakes and fibers. It is also to be understood that unless the filler adds to the strength and stiffness of the composition, it is only a filler and not a reinforcing filler as contemplated herein.

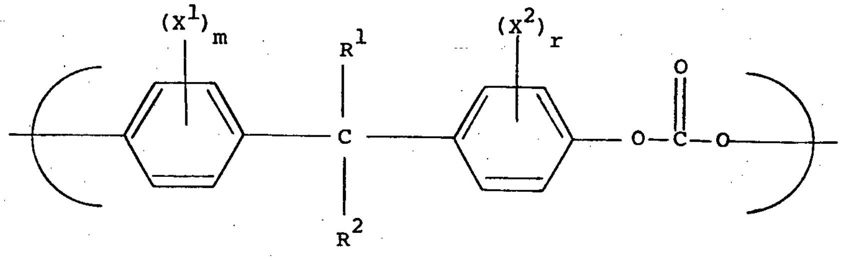
Although it is only necessary to have at least a reinforcing amount of the reinforcement present, in general the reinforced compositions will comprise from 10 to 80% by weight of the total composition of the reinforcing agent.

In particular, the preferred reinforcing fillers are of glass, and it is usually preferred to employ fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively soda-free. This is known as "E" glass. However, other glasses are useful where electrical properties are not important, e.g., the low soda glass known as "C" glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. The filament diameters range from 0.00012 to 0.00075 inch, but this is not critical to the present invention. Glass fibers may be surface coated in accordance with standard procedures to improve their reinforcing performances. In general, best properties will be obtained from reinforced compositions that contain from 15 to 30 percent by weight of the glass reinforced composition.

The length of glass filaments and whether or not they are bundled into fibers and the fibers bundled, in turn to yarns, ropes or rovings, or woven into mats, are also not critical to the practice of the invention. In preparing the present compositions, it is convenient to use the filamentous glass in the form of chopped strands of from 1/8 inch to 1 inch long, preferably less than 1/4 inch long. In articles that are molded from the compositions of the invention, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable, however, because the best properties are exhibited by thermoplastic injection molded articles in which the filament lengths lie between 0.000005 inch and 0.12 (1/8 inch).

The amount of flame retardant additive used is not critical to the invention, so long as it is present in a minor proportion based on said composition—major proportions will detract from physical properties—but at least sufficient to render the polyester resin non-burning or self-extinguishing. Those skilled in the art are well aware that the amount will vary with the nature of the resin and with the efficiency of the additive. In general, however, the amount of additive will be from 0.5 to 50 parts by weight per 100 parts of resin. A preferred range will be from 3 to 25 parts and an especially preferred range will be from 8 to 12 parts of additive per 100 parts of resin. Synergists, e.g., antimony oxide, will be used at 2 to 5 parts by weight per 100 parts of resin.

The flame retardant additives used in the practice of this invention comprise aromatic carbonate homopolymers having repeating units of the formula:



wherein R^1 and R^2 are hydrogen, alkyl or phenyl, X^1 and X^2 are bromine or chlorine and *m* and *r* are from 1 to 4. These materials may be prepared by techniques well known to those skilled in the art. Also used are aromatic carbonate copolymers in which from 25 to 75 weight percent of the repeating units comprise chlorine- or bromine-substituted dihydric phenol units and the remainder of the repeating units comprise dihydric phenol, glycol or dicarboxylic acid units. See, e.g., A. D. Wambach, U.S. 3,915,926, above-mentioned. A particularly preferred flame retardant herein is an aromatic (copoly-) carbonate of 50:50 mole ratio of bisphenol A and tetrabromobisphenol A prepared like Procedure A of U.S. 3,915,926.

The aromatic polycarbonate flame retardants of this invention can also be used with a synergist, particularly inorganic or organic antimony compounds. Such compounds are widely available or can be made in known ways. In preferred embodiments, the type of antimony compound used is not critical, being a choice primarily based on economics. For example, as inorganic compounds there can be used antimony trioxide (Sb_2O_3); antimony phosphate; $KSb(OH)_6$; NH_4SbF_6; or SbS_3. A wide variety of organic antimony compounds can also be used, such as antimony esters with organic acids; cyclic alkyl antimonites; and aryl antimonic acids. Illustrative of the organic antimony compounds, including inorganic salts of such compounds, are: KSb tartrate; Sb caproate; $Sb(OCH_2CH_3)_3$; $Sb(OCH(CH_3)CH_2CH_3)_3$; Sb polymethylene glycolate; or triphenyl antimony. Especially preferred is antimony trioxide.

The process herein by which the talc filler is incorporated into the reinforced flame retarded polyester composition can vary among a wide variety of procedures. For example, in one way, the talc, the reinforcing agent and the flame-retardant are all put into an extrusion compounder with the polyester resin to produce molding pellets. The talc, the reinforcing agent, and flame-retardant are dispersed in a matrix of the polyester resin in the process. In another procedure, the talc, reinforcing agent and flame-retardant are mixed with the polyester resin by dry blending, then either fluxed on a mill and comminuted, or they are extruded and chopped. The talc, reinforcing agent and flame retardant can also be mixed with the powdered or granular polyester and directly molded, e.g., by injection or transfer molding techniques.

It is always important to thoroughly free all of the ingredients; talc, resin, reinforcement, flame-retardant and any optional, conventional additives from as much water as possible.

In addition, compounding should be carried out to ensure that the residence time in the machine is short; the temperature is carefully controlled; the friction heat is utilized; and an intimate blend between talc, the resin, the reinforcement and flame-retardant is obtained.

Although it is not essential, best results are obtained if the ingredients are pre-compounded, pelletized and then molded. Pre-compounding can be carried out in conventional equipment. For example, after carefully pre-drying the polyester resin, talc, flame retardant and the reinforcing agent, e.g., under vacuum at 100°C for 12 hours, a single screw extruder is fed with a dry blend of the ingredients, the screw employed having a long transition section to ensure proper melting. On the other hand, a twin screw extrusion machine, e.g., a 28 mm Werner Pfleiderer machine can be fed with resin and additives (e.g. talc and flame-retardant) at the feed port and reinforcement down stream. In either case, a generally suitable machine temperature will be 450 to 460°F.

The pre-compounded composition can be extruded and cut up into molding compounds such as conventional granules, or pellets, by standard techniques.

The compositions of this invention can be molded in any equipment conventionally used for glass-filled thermoplastic compositions. For example, with poly(1,4-butylene terephthalate), good results will be obtained in an injection molding machine, e.g., of the Newbury type with conventional cylinder temperature, e.g., 450°F and conventional mold temperatures, e.g., 150°F. On the other hand, with poly(ethylene terephthalate), because of the lack of uniformity of crystallization from interior to exterior of thick pieces, somewhat less conventional but still well-known techniques can be used. For example, a nucleating agent such as graphite or a metal oxide, e.g., ZnO or MgO can be included and standard mold temperature of at least 230°F will be used.

The following examples illustrate the invention. They are set forth as a further description but are not to be construed as limiting the invention thereto.

Examples 1 and 2

Dry blends of poly(1,4-butylene terephthalate), intrinsic viscosity, 0.8 dl./g., talc filler, flame retardant, pigment, and glass reinforcement are compounded and extruded. The extrudate is pelletized and injection molded in a 5 oz. Van Dorn machine at 525°F (mold, temperature 150°F). For comparison purposes, reinforced flame-retardant polyester blends without talc are compounded and extruded. The compositions are also moulded into rotors for automotive ignition systems, to serve as test pieces. The formulations used and the physical, electrical and flame-retardant properties obtained are summarized in Table 1.

TABLE 1

Example	1	1A*	1B*	2
Ingredients (parts by weight)				
poly(1,4-butylene terephthalate)	47.7	51.8	62.3	52.7
fibrous glass reinforcement 1/8″	15	30	15	15
aromatic (copoly-) carbonate of bisphenol A and tetrabromobisphenol A	12	13	16.7	12
antimony oxide (Sb_2O_3)	4.5	4.55	6	4.5
talc	20	—	—	15
Carbon black (pigment)	0.5	—	—	0.5
Properties				
Notched Izod impact, ft. lbs./in.	0.64	1.5	1.0	0.72
Tensile strength, psi	11,100	17,000	13,000	11,800
Flexural modulus, psi	1,010,000	1,100,000	730,000	860,000
Heat Deflection Temp. °F 264 psi	—	385	360	—
flame retardancy (UL 94)	V-0	V-0	V-0	V-0
High voltage arc track resistance Track Rate, in/min) UL Bulletin 494)	1.83	11.6	21.0	2.34

*Controls, typical values

The above results demonstrate that the admixture of talc in reinforced flame-retarded polyester compositions drastically improves the arc track resistance compared with the same reinforced flame-retarded polyester compositions which do not contain talc. Moreover, the compositions containing the talc still retain the excellent physical properties of the non-talc containing compositions.

Example 3

The process of Examples 1 and 2 is repeated, including the admixture of poly(ethylene terephthalate) into the composition. The formulation, physical and electrical properties data are summarized in Table 2:

TABLE 2

Example	3
Ingredients (parts by weight)	
poly(1,4-butylene terephthalate)	37.7
poly(ethylene terephthalate) (intrinsic viscosity 0.52)	10
Fibrous glass reinforcement 1/8″	15
Aromatic (copoly-)carbonate of bisphenol A and tetrabromobisphenol A	12
Antimony oxide (Sb_2O_3)	4.5
talc	20
Carbon black (pigment)	0.5
Properties	
Notched Izod impact, ft. lbs./in	0.67
Tensile Strength, psi	11,700
Flexural modulus, psi	980,000
High voltage arc track resistance **(Track Rate, in./min.) (UL Bulletin 494)	1.81

**Molded into distributor rotors and tested.

Obviously, other modifications are possible in view of the above examples. For instance, if the procedure of Example 1 is repeated, substituting for the poly(1,4-butylene terephthalate) the following high molecular weight linear polyesters:

a poly(ethylene terephthalate) having an intrinsic viscosity of about 0.9;

a 60/40 ethylene terephthalate-ethylene isophthalate copolyester having an intrinsic viscosity of about 0.9; or

a poly(1,3-propylene terephthalate) prepared from trimethylene glycol and dimethyl terephthalate and having an intrinsic viscosity of about 1.0 reinforced, flame-retarded polyester compositions according to this invention will be obtained.

Because of their excellent physical, mechanical, chemical, electrical and thermal properties, the compositions of this invention have many and varied uses. The molding powder formulations may be used alone or mixed with other polymers, as well as mold release agents, non-dripping agents, pigments and dyes, and plasticizers.

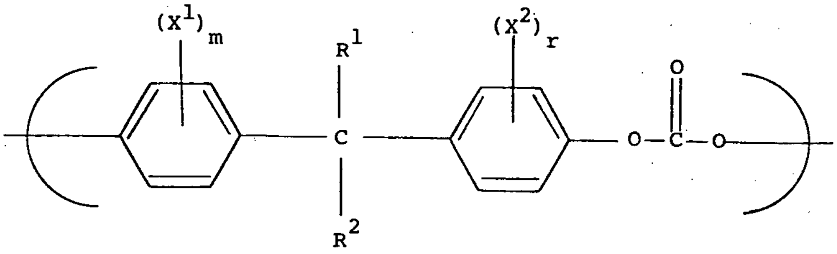
Having regard to the provisions of Section 9 of the Patents Act 1949, attention is directed to the claims of our co-pending British Patent Application No. 50646/77 (Serial No. 1592204).

WHAT WE CLAIM IS:—

1. A flame-retarded reinforced thermoplastic polyester composition which comprises:

(a) a high molecular weight linear polyester resin;

(b) a flame-retardant comprising an aromatic carbonate homopolymer having repeating units of the formula:



wherein R^1 and R^2 are hydrogen, alkyl, or phenyl, X^1 and X^2 are bromine or chlorine and *m* and *r* are from 1 to 4; or an aromatic (copoly-)carbonate in which from 25 to 75 wt.% of the repeating units comprise chlorine- or bromine-substituted dihydric phenol units and the remainder of the repeating units comprise dihydric phenol, glycol or dicarboxylic acid units, or mixtures thereof;

(c) a reinforcing amount of a reinforcing agent; and

(d) talc in an amount sufficient to effect an appreciable increase in the arc track resistance of the composition.

2. A composition as claimed in Claim 1 wherein the flame retardant contains a synergist.

3. A composition as claimed in Claim 2 wherein the synergist comprises 2 to 5 parts by weight per 100 parts by weight of resin.

4. A composition as claimed in Claim 2 or 3 wherein the synergist is antimony trioxide.

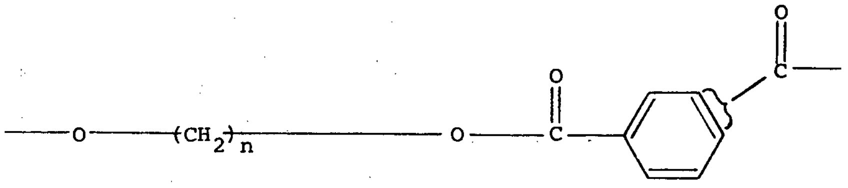
5. A composition as claimed in any preceding claim wherein the talc comprises from 10 to 50% by weight of the total composition.

6. A composition as claimed in Claim 5 wherein the talc comprises from 10 to 30% by weight of the total composition.

7. A composition as claimed in any preceding claim wherein said polyester has an intrinsic viscosity of at least 0.4 deciliters per gram when measured in a solution in a 60:40 mixture of phenol and trichloroethane at 30°C.

8. A composition as claimed in Claim 7 wherein the intrinsic viscosity of the polyester is at least 0.7 deciliters per gram when measured in a solution in a 60:40 mixture of phenol and trichloroethane at 30°C.

9. A composition as claimed in any preceding claim wherein the polyester is a polymeric glycol terephthalate or isophthalate ester having repeating units of the formula:



wherein *n* is 2, 3 or 4, or a mixture of such esters.

10. A composition as claimed in Claim 9 wherein the polyester is poly(1,4-butylene terephthalate) or a mixture of poly(1,4-butylene terephthalate) and poly(ethylene terephthalate).

11. A composition as claimed in any preceding claim wherein the reinforcing agent is glass fibers.

12. A composition as claimed in any preceding claim wherein the reinforcing agent comprises 10 to 80% by weight of the total composition.

13. A composition as claimed in any preceding claim wherein the amount of flame retardant is from 0.5 to 50 parts by weight per 100 parts by weight of resin.

14. A composition as claimed in Claim 13 wherein the amount of flame retardant is from 3 to 25 parts by weight per 100 parts by weight of resin.

15. A composition as claimed in any preceding claim wherein the flame retardant is an aromatic (copoly-)carbonate of a 50:50 mole ration of bisphenol A and tetrabromobisphenol A.

16. A composition as claimed in Claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 3.

17. A process for preparing a thermoplastic composition as claimed in any of Claims 1 to 15 which comprises mixing talc with the high molecular weight linear polyester resin, the reinforcing agent, and the flame-retardant.

18. A process as claimed in Claim 17 and substantially as hereinbefore described with reference to any of Examples 1 to 3.

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