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FLAME-RETARDANT COMPOUNDS AND COMPOSITIONS CONTAINING HALOGEN

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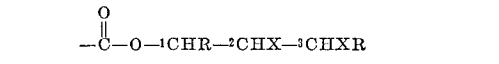
This invention generally relates to novel halogen-containing compounds and particularly concerns poly(2,3-dihaloalkyl) carboxylic esters. Also of special concern are flame-retardant compositions containing these compounds and methods for preparing same.

It is an object of this invention to provide new and useful halogen-containing compounds. Another object is to provide halogen-containing compounds suitable as resin modifiers. A particular object is to provide novel poly (2,3-dihaloalkyl) carboxylic esters. A special object is to provide flame-retardant compositions containing these poly(2,3-dihaloalkyl) carboxylic esters.

These objects and others hereafter mentioned have been accomplished in the discovery of the poly(2,3-dihaloalkyl) carboxylic esters and in the preparation of flame-retardant compositions containing same.

These novel compounds are characterized as having multiple (i.e., at least 2) 2,3-dihaloalkyl carboxylic ester groups.

By the term "2,3-dihaloalkyl carboxylic ester group" is meant a radical having the structural formula:



where "X" is a halogen atom and each "R" is hydrogen or a lower alkyl substituent.

By "halo" or "halogen" is meant the nonmetallic elements of the seventh groups of the periodic system and in particular bromine and chlorine. The halo groups are usually identical (e.g., both halo groups are bromine or both are chlorine, etc.) but can be different (e.g., where one halo is bromine and the other is chlorine, etc.).

The term "lower alkyl substituent" as used above has reference to alkyl groups having no more than 5 carbon atoms (e.g., methyl, ethyl, etc.).

In a much preferred group of esters both the R's are hydrogen. In another preferred system the R at the "1" position is hydrogen and the R at the "3" position is methyl. Also preferred are the compounds where the R at the "1" position is methyl and the R at the "3" position is hydrogen; the compounds where both R's are methyl; and those where the R at the "1" position is hydrogen and the R at the "3" position is ethyl.

The poly(2,3-dihaloalkyl) carboxylic esters included within the present invention can be considered as being composed of 3 sub-groups, i.e., aromatic esters, alicyclic esters and aliphatic esters.

The aromatic esters include those compounds in which the 2,3-dihaloalkyl carboxylic ester groups are attached directly to an aromatic ring, esters in which some of the ester groups are attached to the ring and others in separate side chains, and esters in which all the ester groups are in separate side chains. They may consist of a single benzene ring, a naphthalene ring or other condensed ring system, several aromatic rings singly or doubly linked together or several aromatic rings connected by alkyl rings and/or chains.

Examples include poly(2,3-dihaloalkyl) esters of the following acids: phthalic acid, isophthalic acid, terephthalic acid, 3-methylphthalic acid, 4-tertiarybutylphthalic acid, 3,4-dimethylphthalic acid, 5-methylisophthalic acid, methylterephthalic acid, homophthalic acid, homoisophthalic

acid, homoterephthalic acid, ortho-phenylene diacetic acid, meta-phenylene diacetic acid, para-phenylene diacetic acid, ortho-phenylene acetic-propionic acid, meta-phenylene dipropionic acid, trimesic acid, trimellitic acid, pyromellitic acid, mellophanic acid, prehnitic acid, benzenepentacarboxylic acid, mellitic acid, naphthalic acid, diphenic acid, chrysodiphenic acid, 3,4,9,10-perylenetetracarboxylic acid, etc.

The alicyclic polycarboxylic esters have (2,3-dihaloalkyl) ester groups attached directly to a saturated hydrocarbon ring, ester groups attached to the ring and to separate side chains, or all the ester groups located on separate side chains. These saturated hydrocarbon rings may be otherwise unsubstituted, have alkyl or aryl substituents, and/or be joined to form bicyclic or other higher ring systems.

Suitable esters included within this category may be considered as derivatives of the following acids: cyclopropane-1,1-dicarboxylic acid, cyclopropane-1,1,3-tricarboxylic acid, cyclobutane-1,3-dicarboxylic acid, cyclobutane-1,2,3-tricarboxylic acid, cyclopentane-1,2-dicarboxylic acid, cyclopentane-1,2,3-tricarboxylic acid, cyclohexane-1,1-dicarboxylic acid, cyclohexane-1,2-dicarboxylic acid, cyclohexane-1,3-dicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, cyclohexane-1,3,5-tricarboxylic acid, cyclohexane-1,1,3,3-tetracarboxylic acid, cyclohexane-1,1-diacetic acid, cyclohexane-1-carboxylic-3-acetic acid, camphoric acid, cyclodecane-1,2-dicarboxylic acid, etc.

The aliphatic polyesters of present concern include those compounds having straight or branched saturated hydrocarbon chains. The ester groups may be attached to the same carbon atom or to different carbons.

Specific compounds included within this class may be looked on as esters of the following carboxylic acids: oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, thapsic acid, methylmalonic acid, methylsuccinic acid, alpha,beta-dimethylsuccinic acid, alpha,alpha,beta-trimethylglutaric acid, tricarballylic acid, 1,1,5-pentanetricarboxylic acid, 1,2,4-hexanetricarboxylic acid, methanetetracarboxylic acid, ethane-1,1,2,2-tetracarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, propane 1,1,2,3,3-pentacarboxylic acid, etc.

The polyesters included within the scope of the present invention (whether aromatic, alicyclic, or aliphatic) generally have no more than 30 carbon atoms and, usually, 15 or less. Obviously there will always be at least 8 carbon atoms in the molecule.

The polyesters of this invention whether classified as aromatic, alicyclic or aliphatic often have halogen substituents in the acid portion of the molecule (i.e., halogen elsewhere than in the 2,3-dihaloalkyl groups). In the case of the aromatic polyesters these "additional halo groups" may be located on the aromatic nucleus or its side chains; alicyclic-type esters may have halo groups attached to the ring or side chains; and the aliphatic polyetsers may have halogen atoms on the main chain or branches thereof. As a rule there will not be more than 4 such halogens in the acid portion of the molecult and, commonly, there will only be 2 halogens.

Except for the (2,3-dihaloalkyl) ester groups and possible halogen substitution in the acid portion of the polyester the present compounds are unsubstituted hydrocarbons. There are no free carboxylic acid groups or other functional groups present. Further all alkane rings and chains whether found on aromatic, alicyclic, or aliphatic-type polyesters are fully saturated. The compounds of this invention are further characterized by the fact that generally all (2,3-dihaloalkyl) ester groups are identical.

As a rule the aromatic polyesters are preferred over the alicyclic polyesters and the alicyclic polyesters are in turn preferred over the aliphatic polyesters. Also for certain purposes the compounds containing additional halogen (i.e., halogen in the acid portion of the carboxylic ester) are preferred over the hydrocarbon compounds.

The poly(2,3-dihaloalkyl) carboxylic etsers herein disclosed are conveniently prepared by addition of halogen to the corresponding unsaturated esters. The reaction is generally run at low temperatures (i.e., −25° to +50° C.) using a solvent such as chloroform, carbon tetrachloride, carbon disulfide, acetic acid, diethyl ether, etc. Strong heating is not recommended because it promotes substitution and dehydrohalogenation. For the same reason reaction is usually carried out in the dark. Also it is best to avoid using an excess of halogen. The halogenation reaction is generally complete in approximately 1–6 hours. Often a trace of hydrogen halide is added as a catalyst.

This method is particularly suitable for preparing bromine-containing polyesters. For instance bis(2,3-dibromopropyl) phthalate is obtained from diallyl phthalate on treatment with 2 moles of bromine; bis(2,3-dibromopropyl) succinate is made from diallyl succinate by addition of bromine; etc.

Additions with more reactive gaseous chlorine are also readily accomplished; however, there is more danger of hydrogen substitution than with bromine. Chlorinating agents such as sulfuryl chloride and phosphorus pentachloride are preferred where good yields are difficult to obtain by direct reaction with gaseous chlorine.

Mixed halides (e.g., polyesters containing 2 or more halides) are obtained by using a mixture of halogens to react with the allyl esters. Bromochlorides are for example prepared by the action of bromine and chlorine on olefins.

Where poly(2,3-dihaloalkyl) carboxylic esters are desired having halogen contained in the acid portion of the ester several procedures are possible depending on whether or not these additional halogens are aromatic or alkane substituents.

Direct halogenation on aromatic rings occurs when halogen is introduced in the presence of an ionic catalyst (e.g., ferric halide, aluminum halide, antimony pentahalide, etc.). This process usually is carried out as a separate step after halogen addition to form the poly-(2,3-dihaloalkyl) carboxylic ester groups.

Where it is desired that additional halogens be present as alkane substituents (either on rings or chains) a single step halogenation process is convenient using the corresponding unsaturated hydrocarbon polyester as starting material. For example bis(2,3-dibromopropyl)-4,5-dibromocyclohexane-1,2-dicarboxylate is prepared from diallyl tetrahydrophthalate by single step bromination; bis(2,3-dibromopropyl)-2,3-dibromosuccinate is easily formed by brominating diallyl fumarate; etc.

An alternate general process for preparing any of the compounds of this invention is reaction of the desired polycarboxylic acid or its equivalent (e.g., anhydride, polyester, etc.) with a 2,3-dihaloalkyl alcohol. Esterification is usually effected by refluxing the acid and the alcohol with a small amount of sulfuric acid, hydrochloric acid, or arylsulfonic acid. Equilibrium is shifted to the right by an excess of one of the reactants or by removal of water either by azeotropic distillation or by means of a suitable drying agent.

Flame-retardent compositions containing these new halo esters may be prepared in several ways—the following described compositions and methods being set forth as illustrative.

Natural products are advantageously modified by the present compounds, providing flame-retardant compositions. Prime examples of substances which are beneficially modified are the fibrous cellulosic materials. This

includes, for example, paper, cardboard, pressed board, wood, wood pulp, sawdust, cotton, linen, batting twines, kapok, and regenerated cellulose. The present halogenated compounds are also beneficially used with the natural gums such as agar, gum arabic, tragacanth, gum karaya, etc. Natural rubber and natural resins, such as shellac, copal, damar, pine balsam, rosin, etc., are favorably modified by the halo esters of this invention. Other substances favorably modified by the present compounds are the proteinaceous polymeric materials, such as animal glue, casein, wool, leather, etc.

The present halogenated compounds are advantageously employed as modifiers in synthetic resinous materials. Besides being generally useful as flame-retardants, these dihalo compounds are also useful as plasticizers and facilitate compounding and improve flexibility and other properties of the finished resin. A partial listing of resins advantageously modified by these halo esters is presented below:

(1) *Acrylic resins.*—This group includes polymerized acrylyl and alkacrylyl compounds, such as acrylic acid and methacrylic acid, esters of these acids, acrylonitrile, etc. Special attention is directed towards the polymers prepared from acrylonitrile and the methyl and ethyl acrylates and methacrylates and, also, the acrylonitrile/vinyl chloride copolymers as being particularly suitable for use with the present compounds.

(2) *Cellulose derivatives.*—Included herein are the cellulose esters such as cellulose acetate, cellulose triacetate, cellulose nitrate, cellulose propionate, cellulose acetate butyrate, ethyl cellulose, cellophane, and similar products.

(3) *Coumarone/indene resins.*—These are thermoplastic addition products obtained by heating mixtures of coumarone and indene (such as occur in the light oil fraction from coal tar refining) with acid.

(4) *Epoxy resins.*—These resins are condensation products formed by reaction of a polyhydroxy compound (e.g., ethylene glycol) and epichlorohydrin. Also included herein are the cross-linked products which have been cured with polyacids, polyamines, or the like.

(5) *Furan resins.*—This term refers to homopolymers of furfuryl alcohol, and also to resins obtained by condensation of phenol with furfural or furfuryl alcohol, and to furfural/ketone copolymers. Both cured and uncured resins are advantageously modified by the presently disclosed compounds.

(6) *Melamine resins.*—These are synthetic resins of the thermosetting type, made from melamine and formaldehyde. The lower molecular weight, uncured melamine resins are water soluble syrups; the higher molecular weight materials are less soluble or insoluble and usually solids. All mentioned types are favorably modified by the present halo esters.

(7) *Phenolics.*—These are condensation products produced by reaction of aldehydes (e.g., formaldehyde, acetaldehyde, etc.) with the active hydrogens of phenol or substituted phenols (e.g., cresols or xylenols) which products are usually subsequently heat cured.

(8) *Polyamides.*—These are polymers made by condensation of diamines (or lactams or amino acids) with dibasic acids. Nylon (which is included here) is especially favorably modified by the present compounds.

(9) *Polyesters.*—Usually these synthetic resins are produced by reaction of saturated or unsaturated dibasic acid components such as phthalic anhydride, adipic acid, azelaic acid, maleic anhydride, fumaric acid, etc., with dihydric alcohols such as ethylene, propylene, diethylene, dipropylene, and certain butylene glycols. In a few cases tri-functional monomers such as glycerol or citric acid are used. The modifiers of this invention are particularly useful for treating polyesters prepared from unsaturated dibasic acids as these can be further polymerized through cross-linking. Often another unsaturated monomer such as styrene, vinyl toluene, diallylphthalate, methyl meth-

acrylate, or triallyl cyanurate is used in this second stage.

(10) *Polyalkenes.*—This group includes polyethylene, polypropylene, polyisobutylene, etc. Low and medium-weight polyethylene and solid, high-weight polyethylene, whether of low, medium or high-density are advantageously modified. Similarly the various types of polypropylene and isobutylene are within the scope of this invention. Of special interest are blends of the alkene copolymers with other alkenes (e.g., ethylene/propylene copolymer) or with other unsaturated monomers (e.g., ethylene/vinyl chloride copolymer). [The term alkene copolymer is intended to include polymers where the alkene is present in a major quantity (i.e., 50 percent or more).]

(11) *Polystyrenes.*—Included herein are resins prepared from styrene, nuclear or side chain substituted styrenes (e.g., alpha-methylstyrene), or other vinyl-substituted hydrocarbons (e.g., beta-vinylnaphthalene). The compounds of the present invention give particularly useful products when incorporated into this group of resins.

(12) *Polyurethane resins.*—These are synthetic polymers that may be either thermoplastic or thermosetting and usually are made by action of tolylene diisocyanate or another polyisocyanate with polyols of polyethers or polyesters, or other materials containing hydroxyl groups. Polyurethane foams, flexible and rigid, are particularly beneficially modified with the present halo esters.

(13) *Vinyl resins.*—This comprises a group of thermopolastic resins prepared from monomers having a vinyl linkage. Specifically included herein are polyvinyl acetal, polyvinyl acetate, polyvinyl alcohol, polyvinyl carbazole, polyvinyl chloride, and polyvinyl chloride/acetate. The polyvinyl acetal resins are formed by condensation of acetaldehyde or other suitable aldehyde (e.g., formaldehyde and butyraldehyde) and polyvinyl alcohol.

(14) *Urea-formaldehyde resins.*—Urea and formaldehyde are united in a 2-stage process to form intermediates (methylolurea, dimethylolurea) that are mixed with fillers and converted to thermosetting insoluble infusible resins.

The natural and synthetic materials aforementioned, and others, which will be obvious to those skilled in the art are rendered flame-retardant when contacted with the present halogenated compounds in appropriate proportions. Treatment may be accomplished in several ways.

Finished articles (e.g., paper, cotton, wood, etc.) are conveniently coated or treated with the halides of this invention by employing a volatile solvent such as methyl ethyl ketone, acetone, methanol, diethyl ether, or the like as carriers. Commonly from about 15 to about 60 weight percent solutions are used depending on the type of material, the degree of flame-proofing desired, etc. In practice a 35 weight percent solution is employed as a "rule of thumb." Obviously a carrier is not essential and the halo esters can be applied directly. Treatment varies from about a minute, to an hour, or several days depending on the particular halogenated compound, its concentration, etc., and may be by brushing, spraying or dipping. Whatever method is used treatment is satisfactory is sufficient halo ester is applied to render the material self-extinguishing.

In a preferred procedure particularly suited for modifying synthetic resins the appropriate dihalide is compounded or blended in the material, which is to be modified, during or before final fabrication. Generally the halogenated compounds of this invention are added in quantities which are about 10 to 45 weight percent and, usually, 10 to 30 weight percent, based on the material to be modified. But as little as about 1 to 10 weight percent can be used to give reduced burning rates with certain polymers and, at the other extreme, a 60 weight percent or more is often used for preparing plastisols. Any of the standard compounding or blending methods may be used for incorporating the present halo esters, for example, calendering, casting, extrusion, etc.

EXAMPLE 1

Preparation of bis(2,3-dibromopropyl) phthalate

A solution of 369 g. (1.5 moles) of diallyl phthalate in 200 ml. of carbon tetrachloride is placed in a black-painted flask. A solution of 480 g. of bromine (3 moles) in 200 ml. of carbon tetrachloride is gradually added over a period of 2 hrs. at 3°–6° C. After standing an additional hour at about 5° C., the resulting red solution is poured in a separatory funnel and washed with 300 ml. of 2% aqueous sodium hydroxide. This removes the reddish color. After final washing with water the organic phase is dried over anhydrous magnesium sulfate. The solution is filtered and the filtrate passed through a ¾ x 8 in. column of activated alumina. The carbon tetrachloride is distilled (rotary stripper) at 80°–90° C., under reduced pressure. The slightly turbid viscous residue is filtered through a heated funnel to yield a clear oil which is identified as bis(2,3-dibromopropyl) phthalate.

Analysis.—Calc'd for $C_{14}H_{14}Br_4O_4$: C, 29.7%; H, 2.5%; Br, 56.4%. Found: C, 29.8%; H, 2.5%; Br, 56.2%.

EXAMPLE 2

Preparation of bis(2,3-dibromopropyl) isophthalate

A 1-l. flask is charged with 166 g. (1.0 mole) isophthalic acid, 500 g. (2.29 moles) 2,3-dibromo-1-propanol, 1.0 g. p-toluenesulfonic acid, and 200 ml. toluene. Esterification is carried out at 145° C., for 24 hrs. About 32 ml. water is collected in a water trap. The hot toluene solution is washed with 5% sodium bisulfite. On cooling unreacted isophthalic acid separates and is removed by filtration. After a forerun bis(2,3-dibromopropyl) isophthalate distills at 145° C./0.01 mm.

Analysis.—Calc'd for $C_{14}H_{14}Br_4O_4$: C, 29.7%; H, 2.5%; Br, 56.4%. Found: C, 30.0%; H, 2.6%; Br, 55.9%.

EXAMPLE 3

Preparation of bis(2,3-dibromopropyl) terephthalate

A 2-l. pot fitted with a 12 in. helices-packed column is charged with 70 g. allyl alcohol, 295 g. dimethyl terephthalate, and 3 g. of sodium dissolved in methanol (50 ml.). About 250 ml. methanolallyl alcohol is distilled off during 16 hrs. One l. of hexane is added to the pot and the reaction mixture filtered hot. The filtrate is stripped of hexane and distilled through a 6 x 1 in. Vigreux column. The diallyl terephthalate comes over at 145° C./1.5–2.0 mm.

A 1-l. flask is charged with 124.5 g. (0.50 mole) diallyl terephthalate, 500 g. carbon tetrachloride, and 165 g. (1 mole) bromine at ca. 10° C. (flask cooled with ice bath). After 16 hrs. a 5% solution of sodium bisulfite is added until the color disappears. The reaction mixture is washed with water, 5% sodium bicarbonate solution, and water. After drying over anhydrous magnesium sulfate the solvent is stripped off leaving a milky residue which solidifies on standing. The product is recrystallized from ether with 2% benzene to give bis(2,3-dibromopropyl) terephthalate, M.P. 82°–84° C.

Analysis.—Calc'd for $C_{14}H_{14}Br_4O_4$: C, 29.7%; H, 2.5%; Br, 56.4%. Found: C, 30.1%; H, 2.6%; Br, 55.9%.

EXAMPLE 4

Preparation of bis(2,3-dibromopropyl) 4,5-dibromocyclohexane-1,2-dicarboxylate

A solution of 350 g. (1.4 moles) of diallyl tetrahydrophthalate in 200 ml. of carbon tetrachloride is placed in a 2-l. reaction flask equipped with a paddle stirrer. The solution is cooled to 5°–10° C., and treated with 672 g. (4.2 moles) of bromine in 200 ml. of carbon tetrachloride which is added dropwise over 2 hrs. and 40 min. at 5°–10° C. After stirring an additional hr. at 5°–10° C., the reddish solution is transferred to a separatory funnel,

washed with 200 ml. of 2% aqueous sodium hydroxide, and finally washed with several portions of water. The organic phase is dried over magnesium sulfate and filtered. The solvent is stripped off (rotary stripper at about 80° C./3 mm.). The bis(2,3-dibromopropyl)4,5-dibromocyclohexane-1,2-dicarboxylate is recovered as a pale viscous oil.

Analysis.—Calc'd for $C_{14}H_{18}Br_6O_4$: C, 23.1%; H, 2.5%; Br, 65.7%. Found: C, 23.1%; H, 2.4%; Br, 66.1%.

EXAMPLE 5

Preparation of bis(2,3-dibromopropyl) succinate

A black-painted flask equipped with a mechanical stirrer, a condenser, and an addition funnel is charged with 299 g. (1.5 moles) of diallyl succinate in 200 ml. of carbon tetrachloride. A solution of 480 g. (3 moles) of bromine is added over 2½ hrs. at 5°–7° C. After stirring another hr. at 5° C., the solution is placed in a separatory funnel and washed with 250 ml. of 1% aqueous sodium hydroxide and with water. The solvent is removed under reduced pressure and the liquid residue distilled, B.P. 126°–131° C./1.7–3.5 mm. The slightly turbid distillate is passed through a 4" column of activated alumina to give a pale yellow oil. This material is bis(2,3-dibromopropyl) succinate.

Analysis.—Calc'd for $C_{10}H_{14}Br_4O_4$: C, 23.2%; H, 2.7%; Br, 61.7%. Found: C, 23.2%; H, 2.7%; Br, 61.4%.

EXAMPLE 6

Preparation of bis(2,3-dibromopropyl) 2,3-dibromosuccinate

To a solution of 98 g. (0.5 mole) of diallyl fumarate in 100 ml. of carbon tetrachloride contained in a flask which is painted black is added a soltuion of 240 g. (1.5 moles) of bromine in 100 ml. carbon tetrachloride over 1½ hrs. at 5°–10° C., employing mechanical stirring. After standing for about 12 hrs. the carbon tetrachloride is removed from the reaction mixture by means of a rotary stripper. The resulting yellow oil slowly crystallizes to yield bis(2,3-dibromopropyl) 2,3-dibromosuccinate.

Analysis.—Calc'd for $C_{10}H_{12}Br_6O_4$: C, 17.8%; H, 1.8%; Br, 70.9%. Found: C, 18.3%; H, 1.9%; Br, 70.6%.

EXAMPLE 7

Preparation of tris(2,3-dibromopropyl) trimellitate

A 1-l. flask is charged with 135 g. (0.7 mole) trimellitic anhydride, 218 g. (2.1 moles) 2,3-dibromo-1-propanol, 2 g. p-toluenesulfonic acid, and 250 ml. toluene and heated to reflux. After 24 hrs. 25 ml. water collects in the water trap. The reaction mixture is washed with 5% sodium bisulfite, 5% sodium bicarbonate, and water and then dried over anhydrous sodium sulfate. The toluene solution is passed through an alumina column and the solvent removed under reduced pressure to give tris(2,3-dibromopropyl) trimellitate as a clear viscous liquid.

Anaylsis.—Calc'd for $C_{18}H_{18}Br_6O_6$: C, 26.8%; H, 2.2%; Br, 59.3%. Found: C, 27.1%; H, 2.3%; Br, 58.8%.

EXAMPLE 8

Halogen-containing compounds as modifiers for cellulosic materials

A 35% weight solution of bis(2,3-dibromopropyl) phthalate in methyl ethyl ketone [1] is prepared and paper [2], cotton [3] and wood [4] are soaked therein. The paper and

[1] Any easily volatile solvent can be used in place of the methyl ethyl ketone.

[2] Thin cotton patches are used which are 1½ in. in diameter.

[3] Whatman filter paper No. 3 which is cut in 6 x 2 in. strips is used.

[4] The wood is pine in 6 x ¾ x 1/16 in. splints and previously oven dried.

cotton are submerged for about one minute and the wood is soaked for 15 min. After treatment the impregnated samples are thoroughly dried, tested over a flame, and found to be self-extinguishing [5].

Other runs are conducted using bis(2,3-dibromopropyl) isophthalate and bis(2,3-dibromopropyl) terephthalate and similar results are obtained, i.e., treated paper, cotton, and wood have good flame-retardant properties.

Still other runs are made using tris(2,3-dibromopropyl) trimellitate. Testing confirms that the impregnated samples of paper, cotton, and wood are substantially resistant to burning.

EXAMPLE 9

Flammability of unsaturated polyester containing halogen flame retardants

To 20 g. portions of a polyester resin [6] sufficient flame retardant is incorporated to provide compositions containing each additive in 10%, 11.5% and 25% by weight which are cured by heating in the presence of a free-radical-forming catalyst.[7] Sections of the cross-linked polyester, 3/16 x 1 x 1 in., are supported on a ¼ in. wire mesh 1⅜ in. above a burner. After a sample is ignited [8] for 20 sec. the flame is removed and the sample judged as self-extinguishing (S.E.) or, if the combustion continues, as burnable (B). The self-extinguishing samples are subjected to repeated 15 sec. ignitions. Results are indicated in Table 1.

TABLE 1

Additive	No. of Ignitions	Flammability
Bis(2,3-dibromopropyl) phthalate:		
10%	1	B.
17.5%	1	S.E. 150 sec.
	2	S.E. 90 sec.
25%	1	S.E. 2 sec.
	2	S.E. 3 sec.
	3	S.E. 4 sec.
	4	S.E. 8 sec.
Bis(2,3-dibromopropyl) 4,5-dibromocyclohexane-1,2-dicarboxylate:		
10%	1	B.
17.5%	1	S.E. 8 sec.
	2	S.E. 16 sec.
	3	S.E. 110 sec.
25%	1	S.E. 2 sec.
	2	S.E. 1 sec.
	3	S.E. 4 sec.
	4	S.E. 3 sec.
Bis(2,3-dibromopropyl) succinate:		
10%	1	B.
17.5%	1	S.E. 9 sec.
	2	S.E. 13 sec.
	3	S.E. 11 sec.
	4	S.E. 140 sec.
25%	1	S.E. 68 sec.
	2	S.E. 6 sec.
	3	S.E. 12 sec.
	4	S.E. 2 sec.
Bis(2,3-dibromopropyl) 2,3-dibromosuccinate:		
10%	1	B.
17.5%	1	S.E. 10 sec.
	2	S.E. 15 sec.
	3	S.E. 17 sec.
	4	S.E. 2 sec.
25%	1	S.E. 3 sec.
	2	S.E. 3 sec.
	3	S.E. 3 sec.
	4	S.E. 4 sec.

[5] The ASTM D1692–D59T test or modifications thereof is usually employed.

[6] The polyester resin is prepared by condensing 2.1 moles of propylene glycol, 1 mole of phthalic anhydride, and 1 mole of maleic anhydride to form an unsaturated polyester which is dissolved in ⅓ its weight of styrene.

[7] The preferred catalyst is 50% benzoyl peroxide which is used in 3% by weight based on the unsaturated polyester-styrene mixture.

[8] Ignition temperature is about 900° C.

EXAMPLE 10

Flammability of polystyrene resins containing halogen flame-retardants

The flame retardants (Table 2) are blended with powdered polystyrene in amounts sufficient for the desired percent concentration and the mixture extruded, ground, and compression molded into ⅛ x ⅛ x 4.0 in. bars. Flammability is determined by A.S.T.M. testing procedure D635–56T. By this method the specimen sample is supported on a ⅜ in. wire gauze with about ½ in. of the specimen extending. For each attempt to ignite the specimen a burner [9] is placed so that the tip of the flame just contacts the end of the test specimen. At the end of 30 sec. the flame is removed. The extent of burning is measured along the lower edge of the specimen. If the specimen does not ignite, beyond the 1 in. mark the result is judged to be non-burning (NB). If the specimen burns but the flame goes out before the flame reaches a mark 3 in. from the end which is ignited, it is judged to be self-extinguishing (S.E.). If combustion continues beyond the 3 in. mark, the specimen is judged burnable (B). See Table 2 for results.

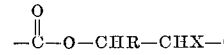
TABLE 2

Additive:	Flammability
Bis(2,3-dibromopropyl) phthalate—	
1.5%	B
2%	NB
4%	NB
6%	NB
Bis(2,3-dibromopropyl) 4,5-dibromocyclohexane-1, 2-dicarboxylate—	
1%	B
2%	S.E.
Bis(2,3-dibromopropyl) succinate—	
3%	B
5%	S.E.
6%	NB
8%	NB
Bis(2,3-dibromopropyl) 2,3-dibromosuccinate—	
2%	B
6%	S.E.

[9] A standard ⅜ in. diameter bunsen burner with air ports open to produce a blue flame approximately 1 in. high is employed.

What is claimed is:

1. A composition of matter comprising a major portion of synthetic resin and a poly(2,3-dihaloalkyl) carboxylic ester of a polycarboxylic acid having from 2 to 6 carboxyl groups in 1–45 percent by weight based on the synthetic resin, said poly-ester having from 8 to about 30 carbon atoms and an ester group structure of the formula

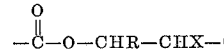


where each X is selected from the group consisting of chlorine and bromine and each R is selected from the group consisting of hydrogen and alkyl groups having from 1 to 5 carbon atoms.

2. The composition of matter of claim 1 where the poly(2,3-dihaloalkyl) carboxylic ester is a bis(2,3-dibromopropyl) carboxylic ester of a phthalic acid.

3. The composition of matter of claim 1 where the synthetic resin is selected from the group consisting of polyesters and polystyrene.

4. A composition of matter comprising a major portion of cellulosic natural product and a self-extinguishing amount of a poly(2,3-dihaloalkyl) carboxylic ester of a polycarboxylic acid having from 2 to 6 carboxyl groups, said poly-ester having from 8 to about 30 carbon atoms and an ester group structure of the formula



where each X is selected from the group consisting of chlorine and bromine and each R is selected from the group consisting of hydrogen and alkyl groups having from 1 to 5 carbon atoms.

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