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- [54] Title: TETRAHALOPHTHALATE ESTERS AS FLAME RETARDANTS FOR CERTAIN RESINS
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- [73] Assignee (s): PENNEALT CORPORATION, of Philadelphia, Pennsylvania, a corporation of Pennsylvania, U. S. A.
- [22] Filed: November 2, 1988
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FOREIGN APPLICATION PRIORITY DATA

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- [51] Int. Class CO8K 5/12
- [58] Field of Search 524/89; 524/217; 524/288; 521/97; 252/609
- [56] Reference (s) Cited and/or Considered:
- | | | | |
|-----------------|-----------|---------|--------------------|
| U. S. Pat. Nos. | 3,966,676 | 6/1976 | Richter et. al. |
| | 4,298,517 | 11/1982 | Sandler |
| | 4,397,977 | 8/1983 | -do- |
| | 4,631,148 | 12/1986 | Braksmayer et. al. |
- [57]

A B S T R A C T

Flame retardant plastic resin compositions with improved flow characteristics containing a tetrahalophthalate ester; the use of the tetrahalophthalate ester as a flame retardant processing aid in a resin; a method for imparting flame retardant and improved flow characteristics to a resin; and a method for manufacturing a flame retardant resin with improved flow characteristics; wherein the resin is selected from among (A) Acrylonitrile-Butadiene-Styrene, (B) Polystyrene, (C) Polycarbonate, and (D) Polybutylene Terephthalate.

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TETRAHALOPHTHALATE ESTERS AS FLAME
RETARDANTS FOR CERTAIN RESINS

ABSTRACT

Flame retardant plastic resin compositions with improved flow characteristics containing a tetrahalophthalate ester; the use of the tetra-
5 halophthalate ester as a flame retardant processing aid in a resin; a method for imparting flame retardant and improved flow characteristics to a resin; and a method for manufacturing a
10 flame retardant resin with improved flow characteristics; wherein the resin is selected from among (A) Acrylonitrile-Butadiene-Styrene, (B) Polystyrene, (C) Polycarbonate, and (D) Polybutylene Terephthalate.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to flame retardant compositions containing at least one tetrahalo-phthalate ester and a certain resin, which is
5 selected from:

(A) Acrylonitrile-Butadiene-Styrene (ABS)

Terpolymer Resins;

(B) Polystyrene Resins;

10 (C) Polycarbonate Resins; and

(D) Polybutylene Terephthalate Resins.

Additionally, the inventive composition may contain one or more brominated and/or chlorinated
15 compounds present in an amount effective to provide additional flame retardancy to the resin.

Statement of Related Art

ABS resins are known in the art as a class
20 of thermoplastics which are characterized by

excellent properties such as chemical resistance, abuse resistance, stain resistance, etc. A discussion of typical properties of ABS resins are described on pages 1-64, 1-66, and 1-68 of

5 Charles A. Harper's "Handbook of Plastics and Elastomers" which is published by McGraw-Hill Book Company in 1975. These pages are hereby incorporated by reference. ABS resins are ter-

10 polymers which are, in general, derived from acrylonitrile, styrene, and butadiene. Most are true graft polymers in which acrylonitrile and styrene are grafted onto a polybutadiene or rubber phase which may further be dispersed in a rigid styrene-acrylonitrile (SAN) matrix.

15 Other ABS resins are mechanical polyblends of elastomeric and rigid copolymer, e.g. butadiene-acrylo-nitrile rubber and SAN. (See G.C. Hawkins, "Condensed Chemical Dictionary", 10th Edition, p. 3, 1981 as well as U.S. Patent Nos.

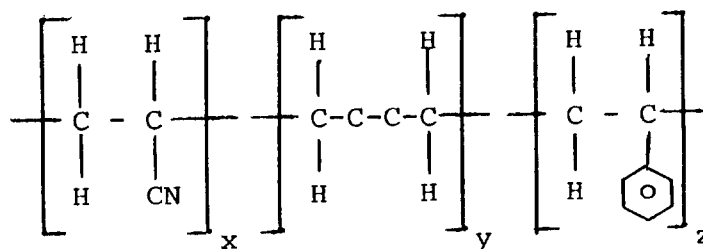
20 4,107,232; 4,206,290; 4,487,886; 4,567,218;

and 4,579,906 all of which are incorporated herein
by reference. Hawkins, supra, defines ABS resin
as: "Any group of tough, rigid thermoplastics
deriving their name from the three letters of the
5 monomers which produce them; Acrylonitrile-
Butadiene-Styrene. Most contemporary ABS are true
graft polymers consisting of an elastomeric poly-
butadiene or rubber phase, grafted with styrene
and acrylonitrile monomers for compatibility,
10 dispersed in a rigid styrene-acrylonitrile (SAN)
matrix. Mechanical polyblends of elastomeric and
rigid copolymers, e.g., butadiene-acrylonitrile
rubber and SAN, historically the first ABS resins,
are also marketed.

15 Varying the composition of the polymer by
changing the ratios of the three monomers and use
of other comonomers and additives results in ABS
resins with a wide range of properties."

The general chemical structure of ABS is:

20



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wherein x, y, and z may independently vary from about 10 to about 1,5000. (See U.S. Patent No. 4,567,218, the teachings of which are incorporated herein by reference.) It should be understood that analogs of each of the monomeric components above may be substituted in whole or in part, and is within the definition of ABS resin. For example, a-methylstyrene may be substituted for styrene and methacrylonitrile for acrylonitrile. Descriptions of the compositions of various ABS resins and how they are prepared may be found in U.S. Patent Nos. 2,505,349; 2,550,139; 2,698,313; 2,713,566; 2,820,773; 2,908,66; 4,107,232; 4,173,561; 4,200,702; 4,206,290; 4,289,687;

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4,355,126; 4,379,440; 4,456,721; 4,487,886; and
4,581,403, the teachings of which are incorpo-
rated herein by reference.

5 The ABS resins are useful in many commercial
applications such as automotive, business machines,
telephone, etc., where high impact strength is
required as well as in the production of molded
articles.

10 Polystyrene resins find extensive use in the
manufacture of packaging material, refrigerator
doors, air conditioner cases; machine housings,
electrical equipment, toys, clock, TV, and radio
cabinets, thermal insulation, ice buckets, con-
tainers, furniture construction, appliances,
15 dinnerware, etc. The preparation and description
of polystyrene and expandable polystyrene are
well known in the art. They are discussed in
G. Hawley, "Condensed Chemical Encyclopedia",
10th Edition, pp 838 and 976 (1981); Kirk-Othmer
20 "Encyclopedia of Chemical Technology", 2nd Edition,

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Vol. 9, pp 847-884 (1966) and Vol. 19, pp
85-134 (1969); A.E. Platt in "Encyclopedia of
Polymer Science and Technology", Vol. 13, pp
156-189 (1970); and U.S. Patent Nos. 4,281,067;
5 4,298,702; 4,419,458; 4,497,911; 4,548,956;
4,596,682; and 4,618,468, the teachings of
which are incorporated herein by reference.

For many applications where styrenic
polymers are used, there is a need to add flame
10 retardants since these materials are flammable.
Some of the applications which require flame
retarded styrenics are radio and TV cabinets,
toys, electrical equipment, furniture construct-
ion, etc. (See, for example, U.S. Patent Nos.
15 4,341,890 and 4,548,956, the teachings of which
are incorporated herein by reference.)

Polycarbonate resins are known in the art
as a class of thermoplastics that are characterized
by excellent properties such as electrical, dimen-
20 sional stability, high impact strength, toughness,

and flexibility. In general, they are prepared by the reaction of a dihydric phenol with a carbonate ester, phosgene, or a bis chloroformate ester. U.S. Patent Nos. 2,999,835;
5 3,169,121; 3,879,348; 4,477,632; 4,477,637;
4,481,338; 4,490,504; 4,532,282; 4,501,875;
4,594,375; and 4,615,832 describe in detail the preparation of various classes of polycarbonate resins, the teachings of which are incorporated
10 herein by reference.

Because of their many excellent properties, polycarbonate resins are useful in many commercial applications as engineering thermoplastics and in the manufacture of molded articles.

15 Polybutylene terephthalate (PBT) resins are known in the art as a class of thermoplastics that are characterized by excellent properties such as thermal stability, good resistance to brittleness, low friction and wear, chemical
20 resistance, etc. In general, they are prepared

by the polycondensation of terephthalic acid
or a diester of terephthalic acid, such as
dimethyl terephthalate (DMT), with 1,4 butanediol.
U.S. Patents 2,645,319; 3,047,539; 3,953,394;
5 and 4,024,102 describe in detail the preparation
of PBT, the teachings of which are incorporated
herein by reference.

The use of brominated and/or chlorinated
compounds by themselves or in combination with
10 other materials such as organic phosphates,
boron compounds, etc. as flame retardants for
ABS resin compositions are well known in the art
and are exemplified by U.S. Patent Nos. 4,051,101;
4,051,105; 4,096,206; 4,107,122; 4,107,232;
15 4,173,561; 4,200,702; 4,289,687; 4,579,906;
4,355,126; 4,378,440; 4,567,218; 4,581,403;
4,581,409; and 4,600,747. The aforesaid patents
are incorporated herein by reference.

Tetrahalophthalate esters have been used as
20 flame-proofing materials. For example, U.S. Patent

No. 4,098,704 describes the use of these materials
as textile finishing agents. U.S. Patent Nos.
4,298,517 and 4,397,977 disclose these compounds as
flame retardants for halogenated resins. However,
5 no teachings have been found which show these
compounds as flame retardants or processing aids
for ABS resins.

SUMMARY OF THE INVENTION

10 This invention encompasses flame retardant
plastic compositions which comprise the following
ingredients in mixture:

(I) a resin which is selected from among:

(A) Acrylonitrile-Butadiene-Styrene

15 (ABS) Terpolymer Resins;

(B) Polystyrene Resins;

(C) Polycarbonate Resins; and

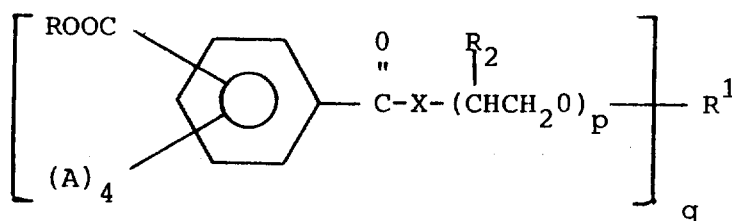
(D) Polybutylene Terephthalate Resins,

and

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(II) a flame retarding effective amount incorporated in the resin of (I) of a tetra-halophthalate ester flame retardant processing aid of the formula:

5



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wherein:

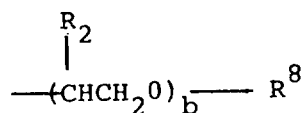
(a) the ring can have all possible isomeric arrangements;

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(b) R is selected from the group consisting of hydrogen, an alkyl or substituted alkyl of 1 to 30 carbons, hydroxyalkyl of 2 to 20 carbons, polyhydroxyalkyl of 3 to 10 carbons,

20

and



5 where R^8 is an alkyl or substituted
 alkyl of 1 to 18 carbons, and b is
 1 to 50;

 (c) R^1 is selected from the group consisting
 of hydrogen, an alkyl or substituted
 alkyl of 1 to 30 carbons, alkenyl or
 10 substituted alkenyl of 2 to 22 carbons,



15 where R^7 is an alkyl of 1 to 18 carbons;
 a polyhydroxyalkyl of 3 to 12 carbons;

20

Preferably, the weight ratio of (I) to (II) is within the range of about 100:1 to about 2:1. (III) Brominated and/or chlorinated flame retardants other than (I) which optionally may be present.

DETAILED DESCRIPTION OF THE INVENTION

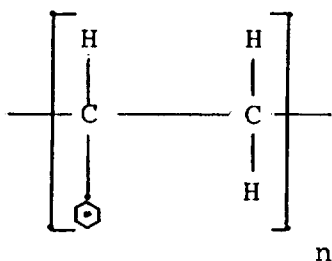
The above composition can also contain other brominated and/or chlorinated flame retardants.

PREFERRED RESINS

(A) In the above ABS resin, a portion or all of acrylic and styrenic monomers comprising the resin include methacrylonitrile or α -methylstyrene, or methacrylonitrile and α -methylstyrene. The preferred ABS resin is comprised of monomeric units of a vinyl aromatic monomer, a vinyl nitrile monomer, and a butadiene monomer and the number of units of each monomer is independently within the range of from about 10 to about 1500.

(B) The polystyrene resin is selected from one of the following:

(a) a homopolymer of styrene having the following repeatable unit



wherein n is within the range of greater than 1 to about 3,000;

15 (b) a homopolymer of styrene as in (a) modified with rubber in which the rubber is dispersed as discrete particles into a matrix of said homopolymer and the weight ratio of

20 rubber to homopolymer is within the

range of from about 2:98 to about
25:75; or

5 (c) a copolymer of butadiene and styrene
in which the weight ratio of butadiene
to styrene is within the range of about
2:98 to about 25:75; or

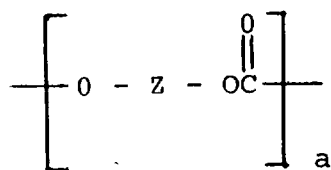
(d) blends of (a) and (b); polybutadiene
and/or a styrene-butadiene copolymer
being preferred.

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In a preferred embodiment of the invention, the
homopolymer of (B) (a) above is in the form of a
polystyrene foam. The foam is preferably prepared
by polymerizing the repeatable homopolymer unit
15 in the presence of a liquid or gaseous blowing
agent and said agent has a boiling point that is
below the softening point of the polystyrene and
does not dissolve said polystyrene. The preferred
blowing agents are selected from the group con-
20 sisting of one or more of propane, butane, pentane,

hexane, heptane, cyclohexane, methyl chloride,
dichlorodifluoroethane, 1,1,2 trifluoroethane,
and 1,1,2 trichloroethane.

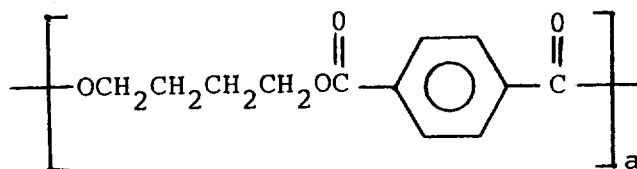
5 (C) The polycarbonate resin has repeated
structural units of the formula:



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wherein a is greater than 1 and z is a divalent
aromatic radical of a dihydric phenol.

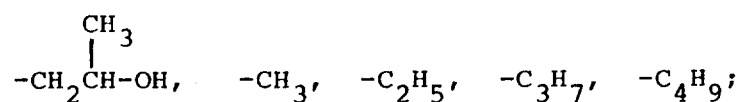
15 (D) The polybutylene terephthalate resins
that may be used in the present invention have
the following repeated structural units of the
formula:



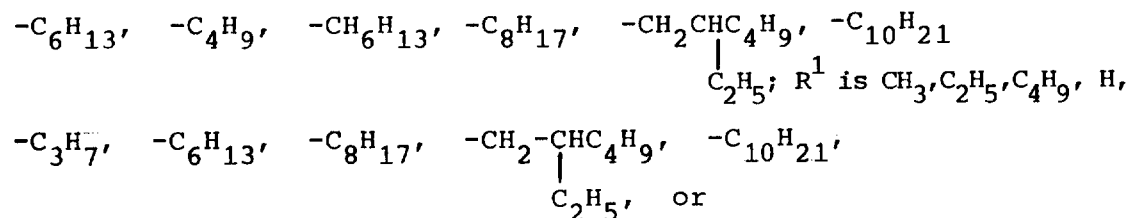
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wherein $a > 1$.

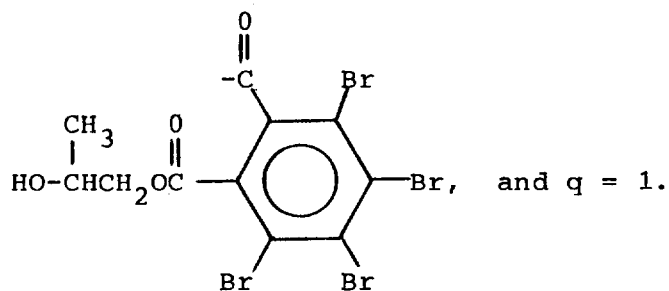
It is preferred that in the above tetra-
halophthalate ester (II), R is an alkyl or
substituted alkyl of 1 to 10 carbons, A is Br,
5 X is oxygen, p is 0 to 20 (most preferably 0),
and q is 1 to 6 (most preferably 1). More
preferably R is



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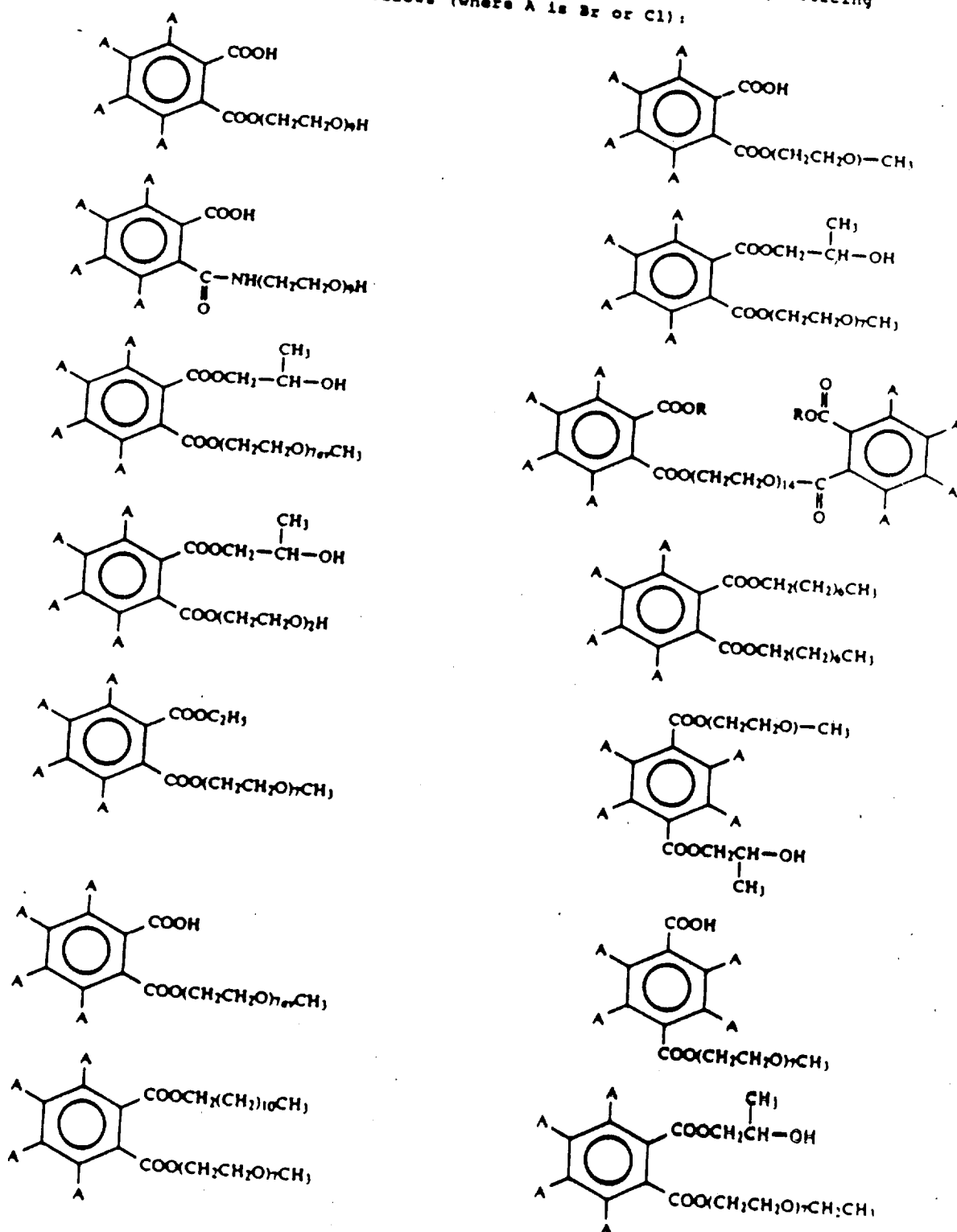
The invention also comprehends a method for preparing a flame retardant plastic composition having enhanced processability properties which comprises incorporating a flame retarding effective amount of one or more of the above tetrahalophthalate esters of (II) in one or more of the above resins.

The invention also comprehends the method of improving the flame retardancy, processability, and physical properties such as impact strength of the specified resins by incorporating in the resins the tetrahalophthalate compounds as described above alone or in combination with other bromine and/or chlorinated flame retardants.

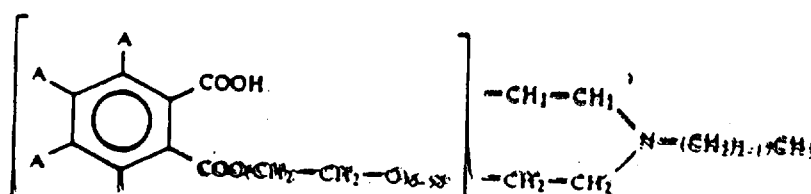
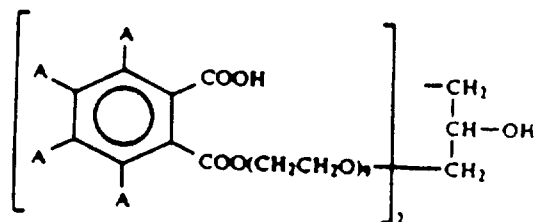
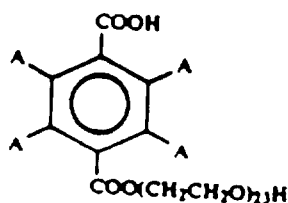
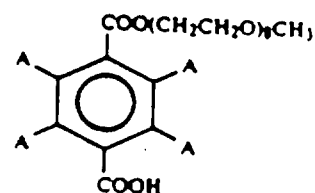
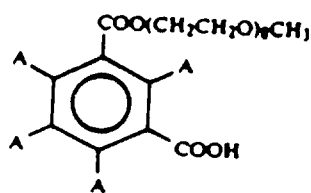
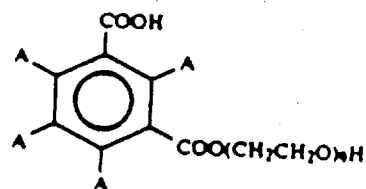
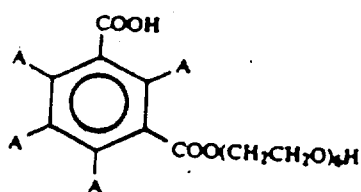
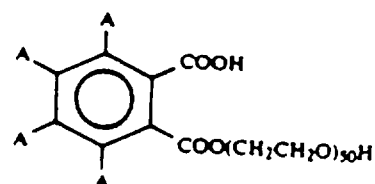
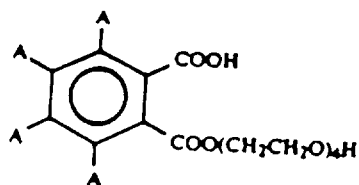
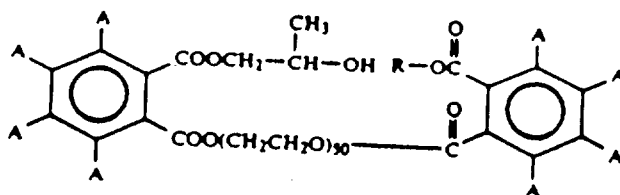
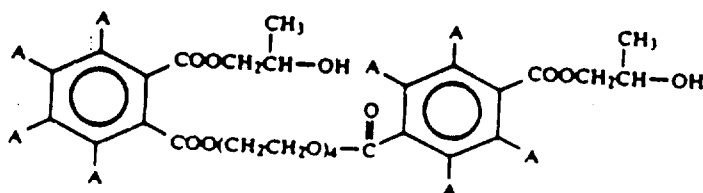
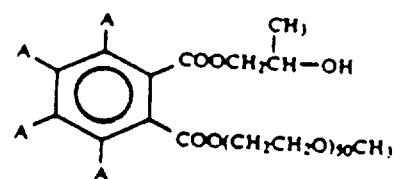
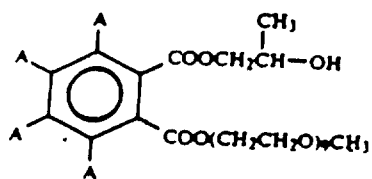
The above resins are sold on the basis of their impact properties. Unfortunately, when such materials have to be flame retarded with conventional retardants to meet code requirements, there is a significant loss of impact strength.

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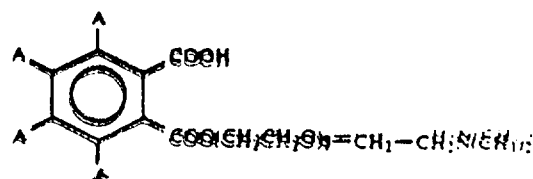
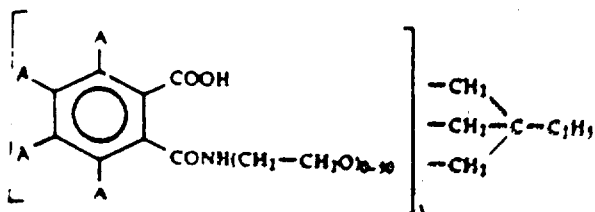
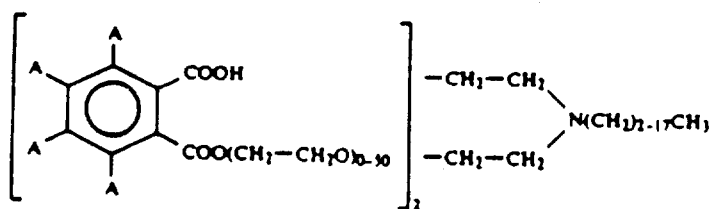
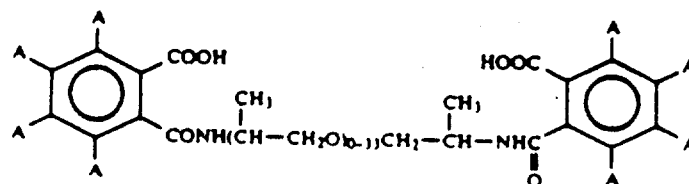
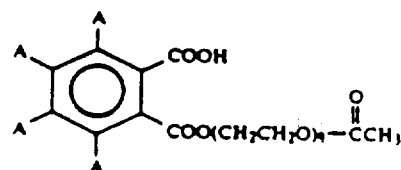
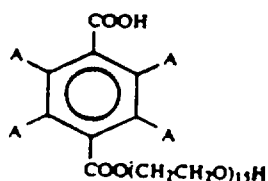
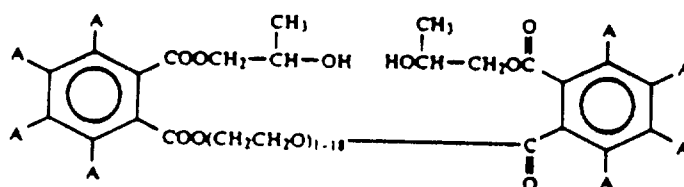
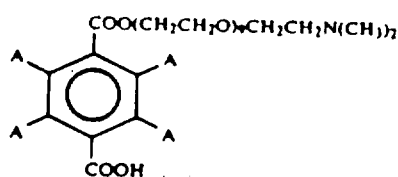
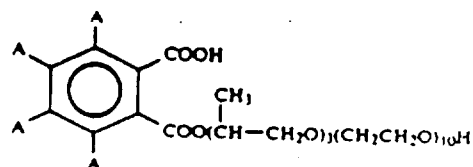
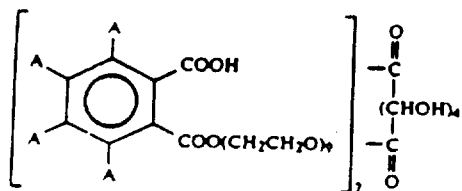
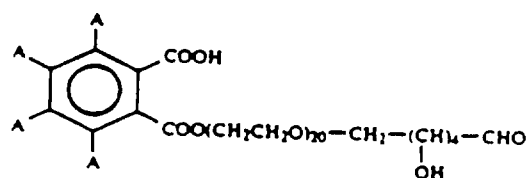
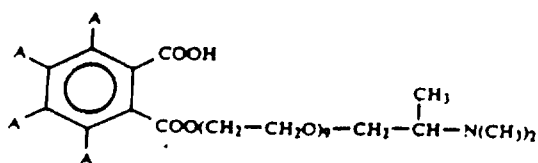
Representative tetrahalophthalate compounds useful in practicing this invention are as follows (where A is Br or Cl):

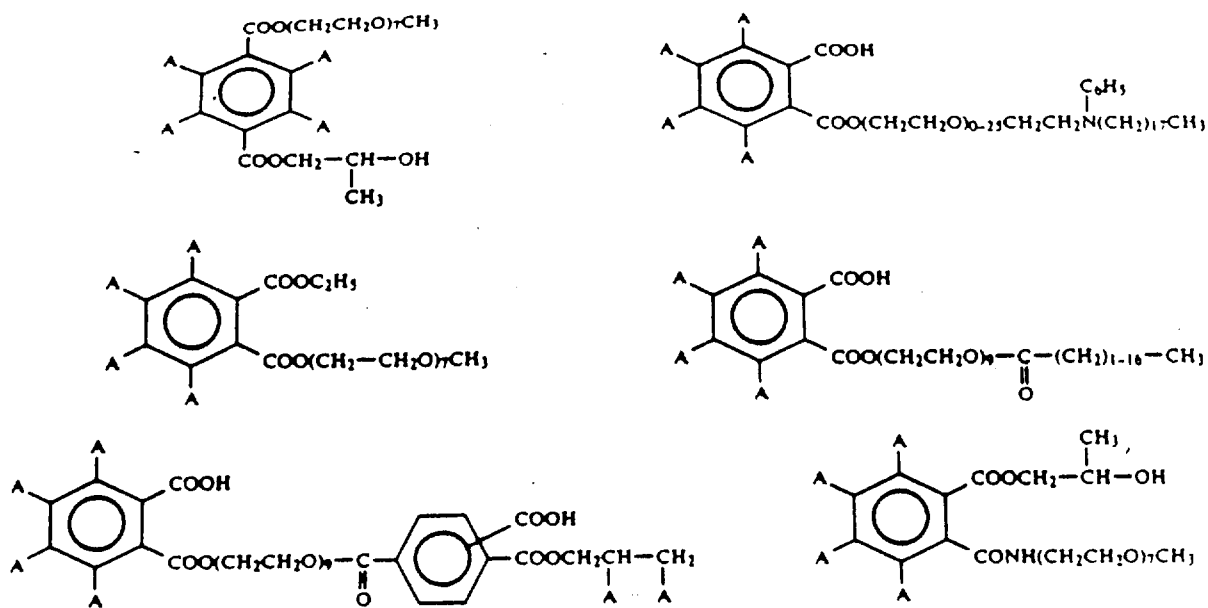


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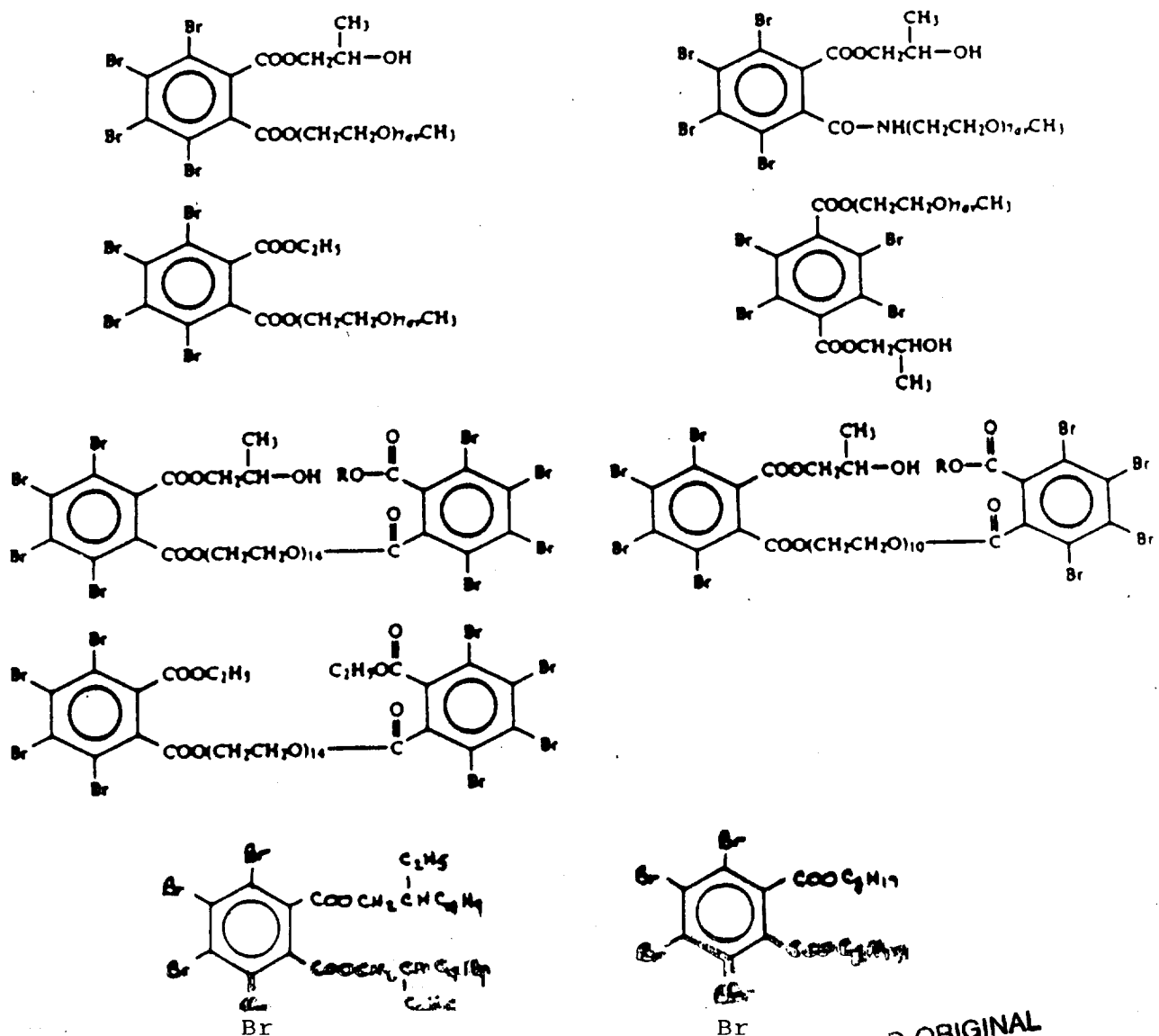


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The preferred compounds are:



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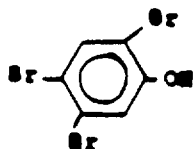
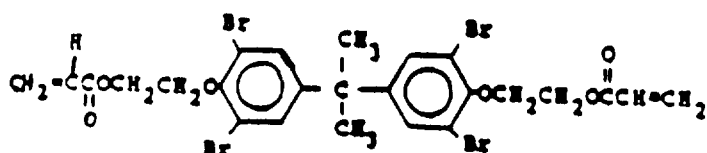
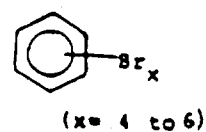
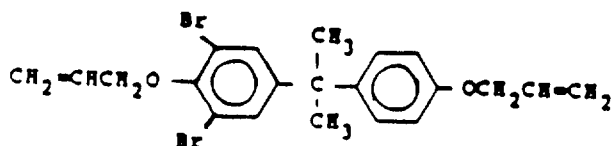
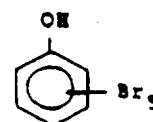
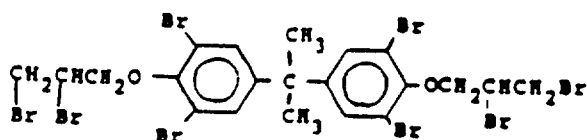
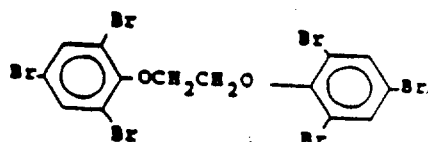
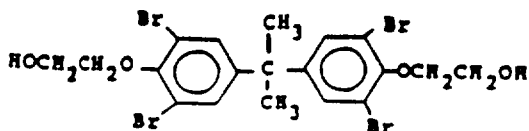
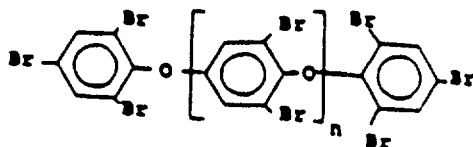
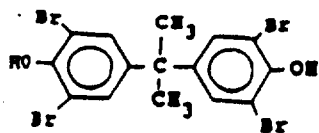
The R in the above formulas is $\text{-CH}_2\text{-}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-OH}$

or $\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-OH}$.

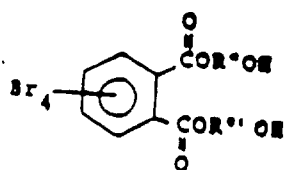
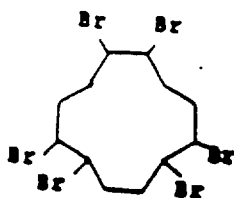
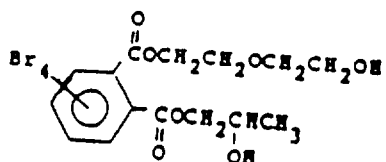
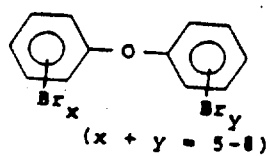
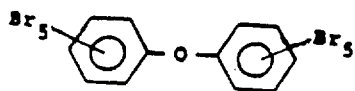
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The brominated and/or chlorinated compounds that may be used in combination with the tetra-halophthalates are any of those that are well known in the art. Preferred halogenated flame retardant examples are:

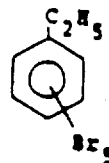
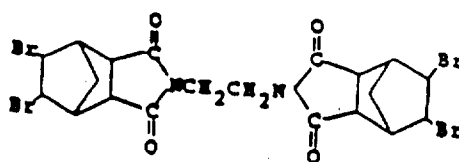
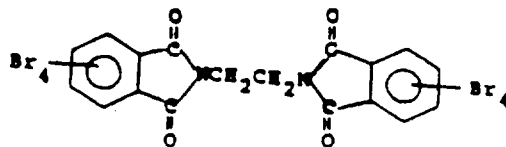
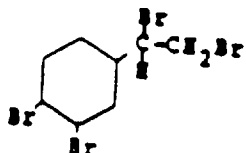
10



BAD ORIGINAL



where R' and R'' are
alkylene or substituted alkylene



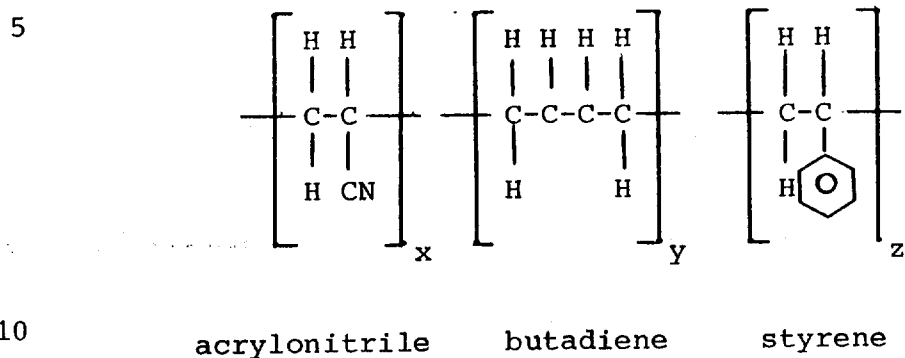
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In practicing this invention, (II) the tetrahalophthalate by itself or additionally with (III) other brominated and/or chlorinated flame retardants is added to (I) the resin in any convenient manner, such as blending or extruding in order to get a uniform composition. Flame retardant synergists such as antimony oxide (Sb_2O_3) may also be added if desired. In addition, other additives such as thermal stabilizers, ultraviolet stabilizers, reinforcing agents, organic polymers, mold release agents, blowing agents, colorants, and the like may also be optionally included. A further advantage of the tetrahalophthalates alone or in combination with other brominated and/or chlorinated compounds as used in this invention is their improved compatibility with the resins.

Detailed Resin Descriptions

(A) The ABS resins that may be used in this

invention are, in general, derived from acrylonitrile, styrene, and butadiene and have the following general structure:



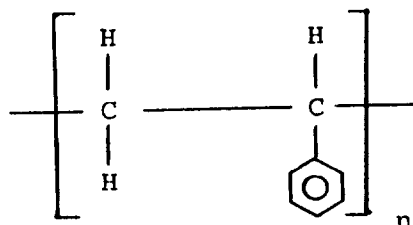
wherein x, y, and z may independently vary from about 10 to about 1,500. It is understood that
 15 analogs of each of the components above that
 comprise the ABS resins may be substituted in
 whole or in part.

 The ratio of tetrahalophthalate or a mixture
 of tetrahalophthalate and one or more brominated
 20 and/or chlorinated compounds to ABS resins that

will impart flame retardancy to the latter may vary from 1:100 to about 1:2 depending on the application. In addition, the ratio of tetrahalophthalate to other brominated and/or chlorinated compounds may vary from 100:0 to about 1:99.

(B) The styrenic resins that may be used in the present invention are the following: polystyrene homopolymer, both crystalline and non-crystalline forms; expandable polystyrene beads, and rubber-modified polystyrene which include medium impact polystyrene, high impact polystyrene (HIPS), and super high impact polystyrene.

The homopolymers of styrene, both crystalline and non-crystalline, have the following repeatable unit:



wherein n is greater than 1 to about 2000-3000.
The non-crystalline forms are generally prepared
by polymerizing styrene with peroxide catalyst
such as those described in U.S. Patent No.
5 4,281,067 while the crystalline stereoregular
isotactic form uses Ziegler-Natta catalysts
(See I. Pasquon in Encyclopedia of Polymer
Science and Technology, Vol. 13, pp. 14, 19-20,
and 31 (1970)).

10 Expandable polystyrene beads are those that
are prepared by incorporating a volatile ex-
panding or blowing agent during the polymerization
of styrene. The blowing or expanding agents that
may be used to cause polystyrene to foam are
15 well known in the art. They may be liquid or
gaseous, do not dissolve the styrene polymer, and
have boiling points below the softening point of
the polymer (See Column 6 in U.S. Patent No.
4,618,468). Suitable blowing agents are aliphatic
20 hydrocarbons such as propane, butane, pentane,

hexane, heptane, cyclohexane or halogen hydrocarbons such as methyl chloride, dichlorodifluoromethane, 1,1,2 trifluoroethane, 1,1,2 trichloroethane and the like. Mixtures of the above may
5 also be used. Typically, expanding agents are used in amounts of about 2 to 20% by weight.

Rubber-modified polystyrenes that are suitable include medium, high, and super high impact polystyrenes. In these compositions,
10 the rubber is dispersed in the polystyrene matrix as discrete particles (See U.S. Patent No. 4,341,890). Many rubber-modified styrenes are prepared by polymerizing styrene in the presence of a rubber such as polybutadiene or
15 a styrene-butadiene copolymer (SBR). Some grafting of the styrene to the rubber takes place during polymerization. The weight ratio of the rubber to polystyrene may vary from about 2:98 to about 25:75. In general, the moderate
20 impact polystyrene will contain about 2 to about

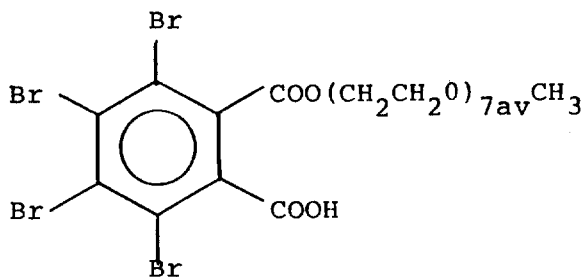
4% rubber, the high impact polystyrene greater than about 10% to about 25%. [See H. Keskkula in "Encyclopedia of Polymer Science and Technology" Vol. 13, pp. 396 and 400-404 (1970)]⁷.

5 (C) The polycarbonate resins that may be employed in the present invention are typical dihydric phenols such as used are disclosed in U.S. Patent No. 3,334,154, which is incorporated herein by reference. They are as follows:

10 2,2 bis-(4-hydroxyphenyl)-propane; hydroquinone;
resorcinol, 2,2 bis-(4-hydroxyphenyl)-pentane;
2,4' dihydroxydiphenyl methane;
bis-(2-hydroxyphenyl)-methane;
bis-(4-hydroxyphenyl)-methane;
15 bis-(4-hydroxy-5-nitrophenyl)-methane;
1,1 bis(4-hydroxyphenyl)-ethane;
3,3 bis-(4-hydroxyphenyl)-pentane;
2,2' dihydroxydiphenyl sulfone;
4,4' dihydroxydiphenyl ether; and
20 4,4' dihydroxy-2,5-diethoxydiphenyl ether.

EXAMPLE 1

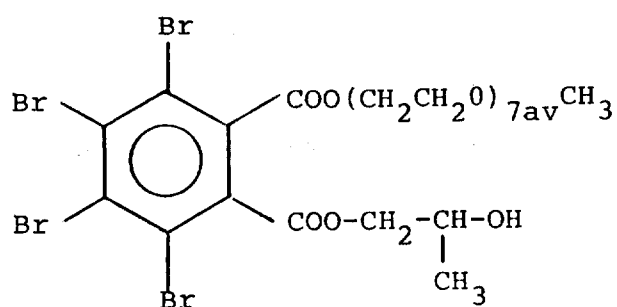
To 1,392 g (3.0 moles) of tetrabromophthalic anhydride were added 1,050 g (3.0 moles) of Methoxy Carbowax 350 in the presence of 22.0 g of sodium acetate. The mixture was heated at 90°C for 9 hours in a nitrogen atmosphere. The reaction mixture was filtered hot to remove the sodium acetate. The analytical data were consistent with the assigned structure.



EXAMPLE 2

To the compound of Example 1 were added 348.0 g (6.0 moles) of propylene oxide and 2.0

liters of toluene. The mixture was heated at 60°-100°C. The solvent and residual propylene oxide were removed to give the product in almost quantitative yield. The analytical data were consistent with the assigned structure:



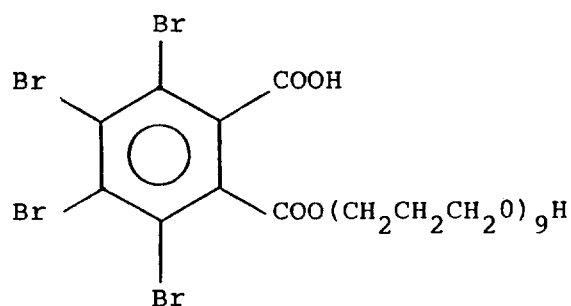
EXAMPLE 3

To 92.8 g (0.2 mole) of tetrabromophthalic anhydride is added all at once 80 g (0.2 mole) of Carbowax 400 and the mixture heated to 120°-130°C for 2.5 hours. The desired product is isolated in essentially quantitative yield as a

clear yellow viscous liquid. Calcd. Mol. Wt.,
864; found 865. Calcd. % Br. 37.1; found, 38.5.
The analytical data are consistent with the
assigned structure:

5

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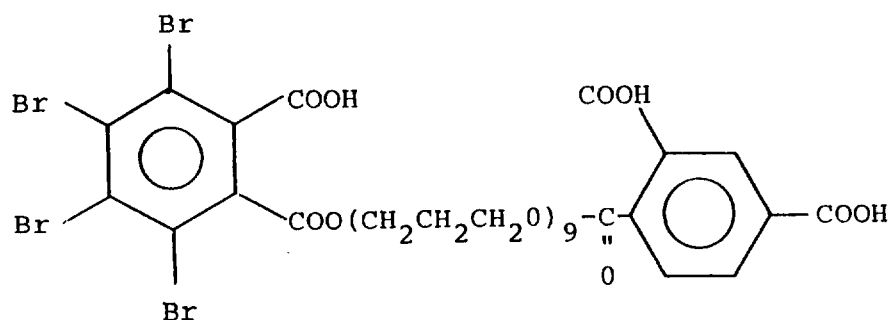
EXAMPLE 4

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To 240 g (0.24 mole) of the compound of
Example 3 is added 45.3 g (0.24 mole) of tri-
metallic anhydride and heated at 155°C under
nitrogen for about 7 hours. The infrared
spectrum indicated the completion of the
reaction by the substantial disappearance of the

anhydride absorption band at 5.65. The product was isolated in essentially quantitative yield. Analy. Calcd.; %Br, 30.3%; Mol. Wt. 1056; neutralization equivalent, 352; Found: %Br, 29.4; Mol. Wt., 1014; neutralization equivalent, 351. The spectral data was consistent with the structure:



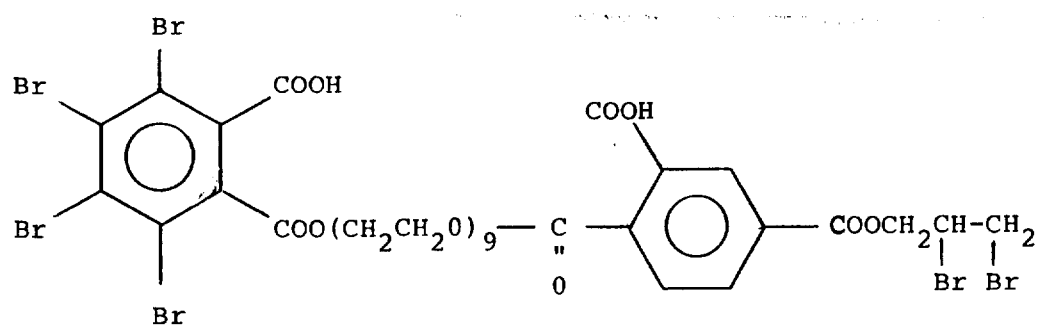
EXAMPLE 5

To 156.3 g (0.18 mole) of the compound of Example 3 is added 70.9 g (0.18 mole) 2,3-dibromopropyl trimellitate. The mixture is heated at

130°-140°C for 6 hours with stirring to give the product as a brown opaque oil. Isolation afforded the product in essentially quantitative yield and the analysis is consistent with the structure being:

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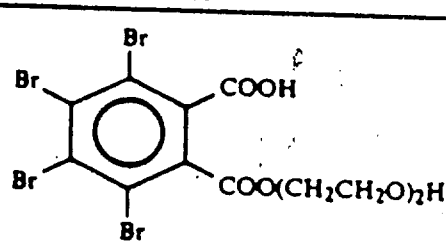
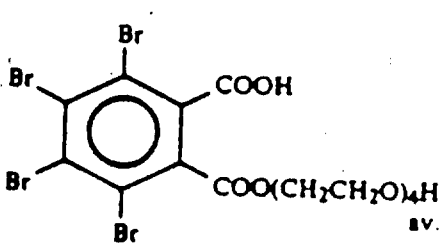
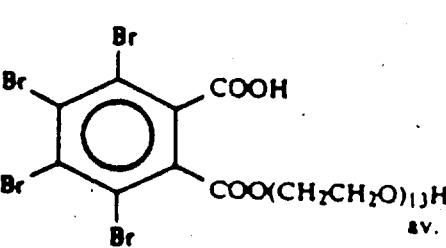
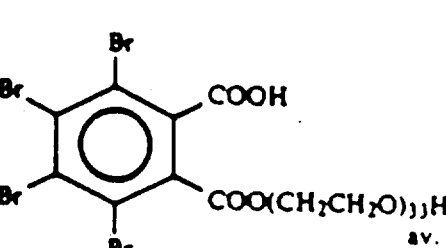


(and isomers)

15

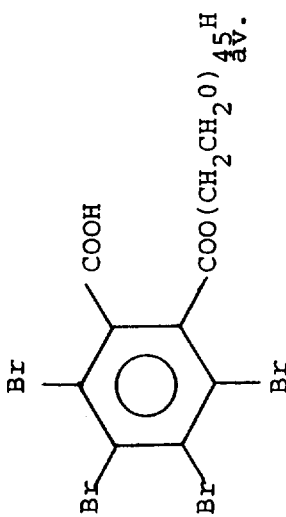
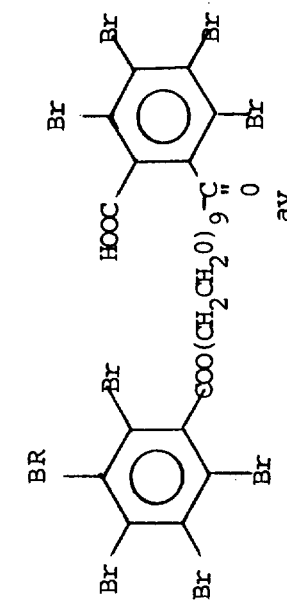
Examples 6 to 11

The following preparation were carried out as in Example 1 using the reactant set forth below.

Example No.	Tetrabromophthalic Anhydride	Hydroxy Compound	Product Structure
6	1.0 mole	HOCH ₂ CH ₂ OCH ₂ CH ₂ OH 1.0 mole	
7	1.0 mole	HO(CH ₂ CH ₂ O) ₄ H (Carbowax 200) 1.0 mole	
8	1.0 mole	HO(CH ₂ CH ₂ O) ₁₁ H (Carbowax 600) 1.0 mole	
9	1.0 mole	HO(CH ₂ CH ₂ O) ₂₁ H (Carbowax 1000) 1.0 mole	

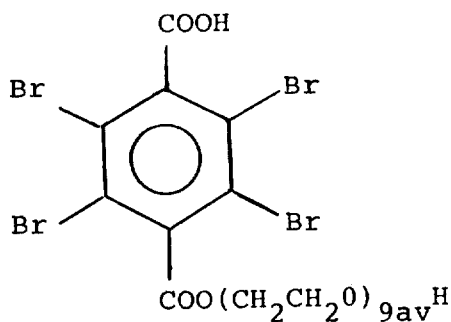
EXAMPLES 6 to 11 - continued

The following preparation were carried out as in Example 1 using the reactant set forth below.

Example No.	Tetrabromophthalic Anhydride	Hydroxy Compound	Product Structure
10	1.0 mole	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{45}\text{H}$ (Polyglycol E-2000) 1.0 mole	
11	2.0 mole	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_9\text{H}$ (Carbowax 400) 1.0 mole	

EXAMPLE 12

To 96.4 g (0.2 mole) of tetrabromoterephthalic acid is added all once 160 g (0.2 mole) of Carbowax 400 and 300 g toluene containing 1.0 g P-toluene sulfonic acid. The mixture is heated to reflux until 3.6 g (0.2 mole) water was collected. The toluene is removed under reduced pressure to give a clear viscous liquid in essentially quantitative yield.



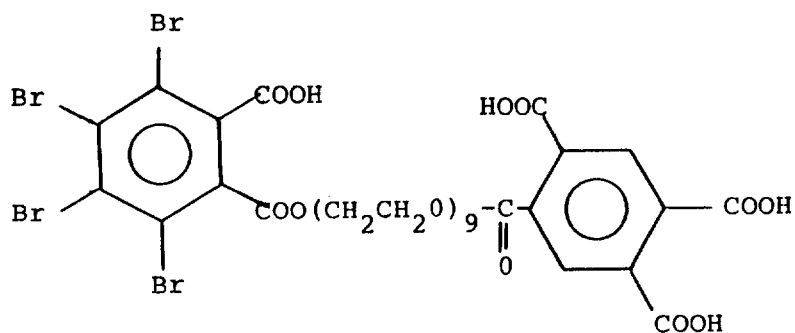
EXAMPLE 13

To 86.4 g (0.1 mole) of the compound of



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Example 3 is added all at once 21.8 g (0.1 mole)
pyrometallitic dianhydride and the mixture heated
to 120°-130°C for 2.5 hours to give the desired
product. Water, 1.8 g(0.1 mole), is added to
open the remaining anhydride group and the
analytical data are consistent with the assigned
structure:

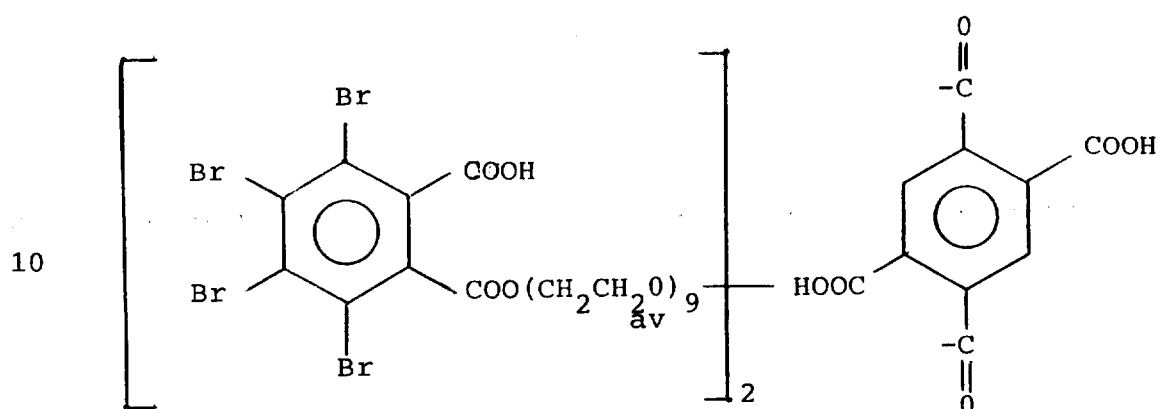


EXAMPLE 14

To 86.4 g (0.1 mole) of the compound of
Example 3 is added all at once 10.9 g (0.05 mole)

of pyromellitic dianhydride and the mixture heated to 120°-130°C for 2.5 hours to give the desired product. The analytical data are consistent with the assigned structure:

5



15

(and isomers)

EXAMPLE 15

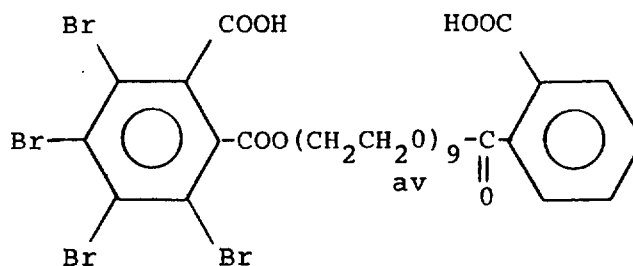
To 86.4 g (0.1 mole) of the compound of Example 3 is added all at once 21.8 g (0.1 mole)

20

of phthalic anhydride and the mixture heated to 120°C-130°C for 2.5 hours to give the desired product. The analytic data are consistent with the assigned structure:

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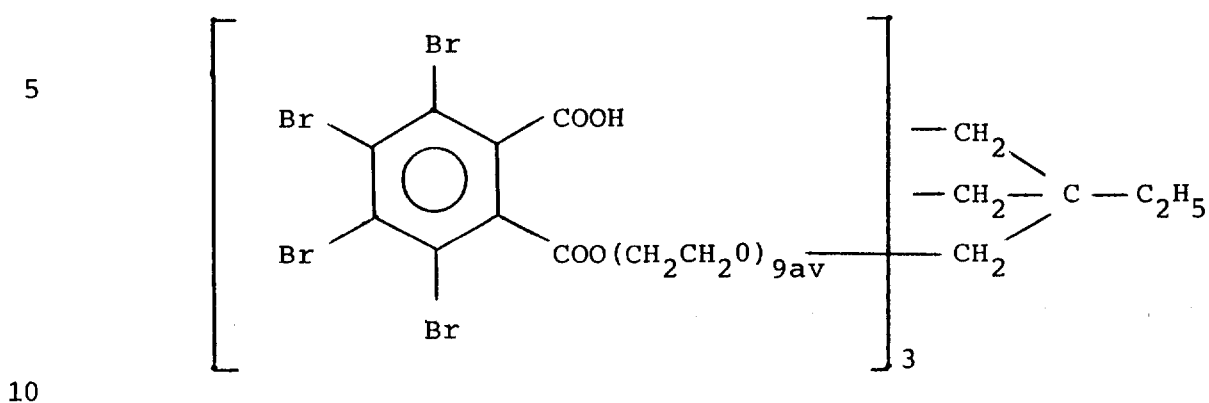
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EXAMPLE 16

20

To 139.2 g (0.3mole) of tetrabromophthalic anhydride is added all at once 122.9 g (0.1 mole) polyoxyethylated trimethylol propane of molecular weight 1229 and the mixture heated to 120°-130°C for 2.5 hours to give the desired product. The

analytical data are consistent with the assigned structure:

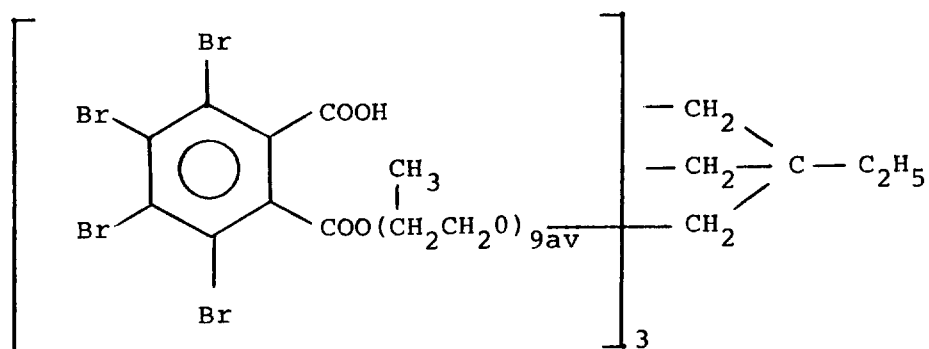


EXAMPLE 17

15 To 139.2 g (0.3mole) of tetrabromophthalic anhydride is added all at once 156.8 g (0.1 mole) polyoxypropylated trimethylol propane of molecular weight 1568 and the mixture heated to 120°-130°C for 2.5 hours to give the desired product. The analytical data are consistent with the assigned structure:

20

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EXAMPLE 18

15

To 284.0 g (1.0 mole) of tetrachlorophthalic anhydride is added 350.0 g (1.0 mole) of Methoxy Carbowax 350 in presence of 7.0 g of sodium acetate. The mixture is heated at 90°C for 8 hours in a nitrogen atmosphere. The reaction mixture is filtered hot to remove sodium acetate to give the expected product in nearly quantitative yield. The analytical data are consistent with the assigned structure:

20

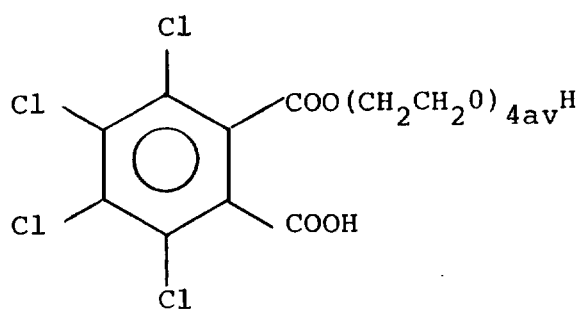
EXAMPLE 19

To 634.0 g (1.0 mole) of the composition of Example 18 is added 116 g (2.0 moles) of propylene oxide in 200 ml of toluene. The reaction mixture is heated from 60°-100°C for 3-5 hours, and then concentrated to give the product in nearly quantitative yield. The analytical data are consistent with the assigned structure:

CC(C)COC(=O)c1cc(Cl)c(Cl)c(Cl)c1C(=O)OCCOC

EXAMPLE 20

20



10 EXAMPLE 21

To 484.0 g (1.0 mole) of the product of Example 21 is added 116.0 g (2.0 mole) of propylene oxide in 200 ml of toluene. The reaction mixture is warmed at 60°-100°C for 3-5 hours, and then concentrated to give the product in nearly quantitative yield. The analytical data are consistent with the assigned structure:



EXAMPLE 22

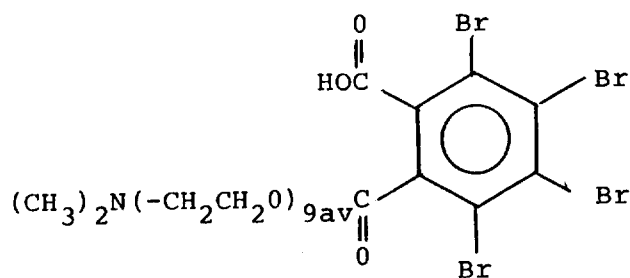
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[illegible]

EXAMPLE 23

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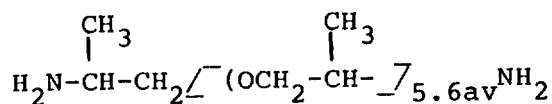


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EXAMPLE 24

To 92.8 g (0.2 mole) of tetrabromophthalic anhydride is added 80 g (0.2 mole) of

15



20

(Jeffamine D-400) and the mixture heated to about 120°C. The final product is obtained in almost quantitative yield. The analytical data are consistent with the assigned structure:

O=C(O)c1cc(Br)cc(Br)c1CNC(C)CCOC(C)OCCN

EXAMPLE 25

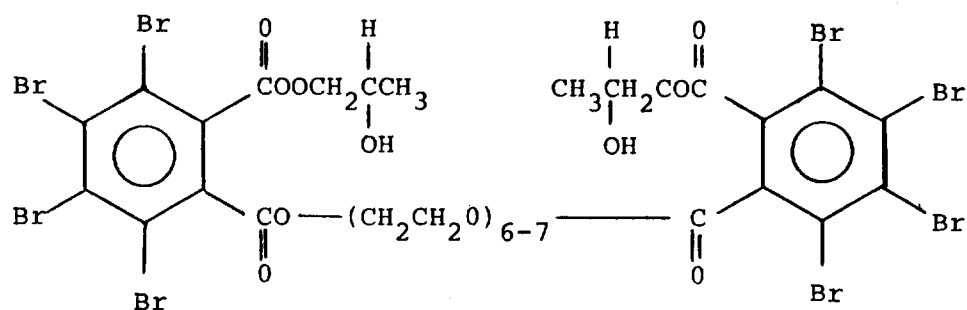
Poly(ethylene glycol 300), 204.5 g (0.67 mole) was refluxed ($T = 117^{\circ}\text{C}$) with 600 ml of toluene for 1.5 hours in order to remove a small amount of water present in the glycol. The mixture was cooled to about 100°C and tetrabromophthalic anhydride, 614.5 g (1.35 moles) and sodium acetate, 1.62 g were added and the mixture was reheated to reflux and held for 25 hours. After the mixture was cooled to 50°C , propylene oxide, (156.4 g, 2.69 moles, 100% excess)

was added and the mixture heated to and held at 100°C for 2.5 hours. When the solution cooled to about 50°C, it was filtered through a bed of diatomaceous earth and decolorizing charcoal.

5 The filtrate was distilled to remove the solvent to give 904.1 g of product as a viscous liquid. Calcd. % Br, 47.4. Found % Br, 46.5. Analytical data is consistent with the assigned structure.

10

15



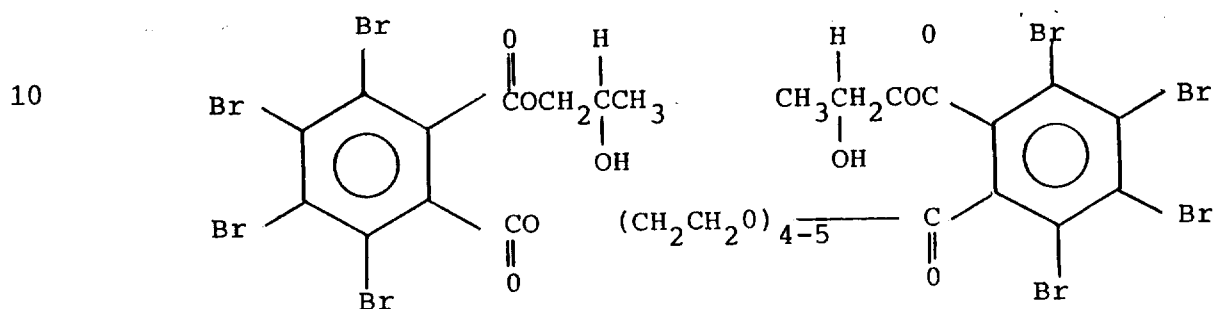
EXAMPLE 26

20

This compound was prepared by the procedure

described in Example 25 except that poly-
 (ethylene glycol 200) was used in place of
 poly(ethylene 300). Product is viscous liquid.
 Calcd. % Br, 51.0. Found % Br. 49.3.

5 Analytical data was consistent with the assigned
 structure.



EXAMPLE 27

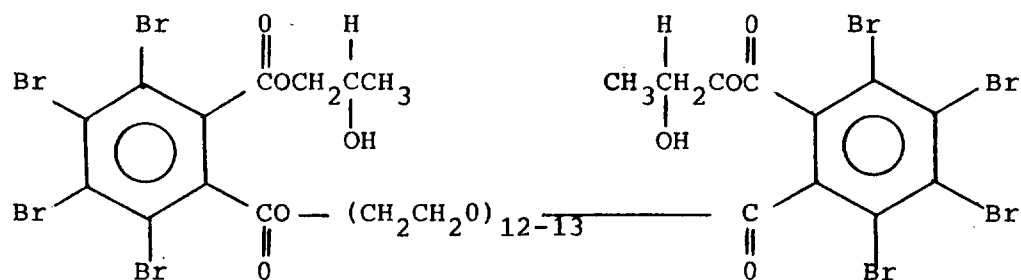
This compound was prepared by the procedure
 described in Example 25 except that poly(ethylene
 glycol 600) was used in place of poly(ethylene
 20 glycol 300). Product is a viscous liquid.

Calcd. % Br. 39.5. Found % Br. 39.3.

Analytical data is consistent with the assigned structure.

5

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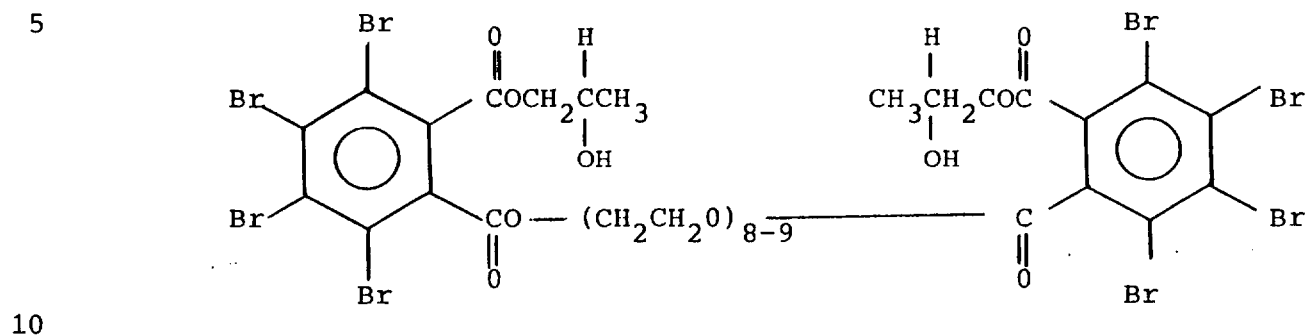
EXAMPLE 28

This compound was prepared by the procedure described in Example 25 except that poly(ethylene glycol 400) was used in place of poly(ethylene glycol 300). Product is a viscous liquid.

20

Calcd. %Br. 44.2. Found % Br. 44.9.

Analytical data is consistent with the assigned structure.

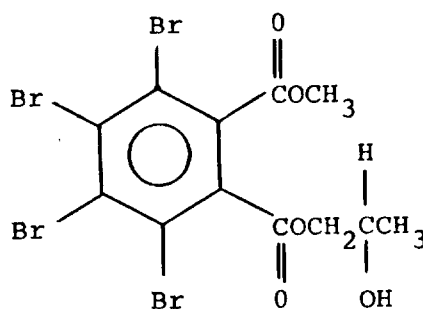


EXAMPLE 29

15 Methanol (54.1 g, 1.5 mole), tetrabromophthalic anhydride (695.6 g, 1.6 moles), and potassium acetate, 2.73 g were refluxed for 4 hours with 500 ml of toluene. After cooling the reaction mixture to room temperature, propylene

20 oxide (87.12 g, 1.5 moles) were added and the

mixture reacted at 80°C for 2.5 hours. Product was obtained as a viscous liquid after distilling out the toluene. Calcd. % Br. 57.7. Found % Br, 57.2. Analytical data is consistent with assigned structure.



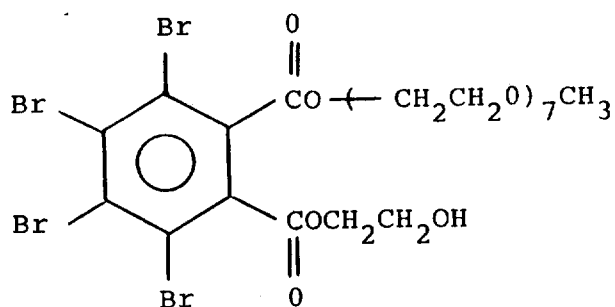
EXAMPLE 30

This compound was prepared by the procedure similar to that described in Example 29 except that methoxycarbowax 350 was used in place of

methanol and ethylene oxide in place of propylene oxide. Calcd. % Br, 37.8. Found % Br, 37.2. Analytical data is consistent with assigned structure.

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EXAMPLE 31

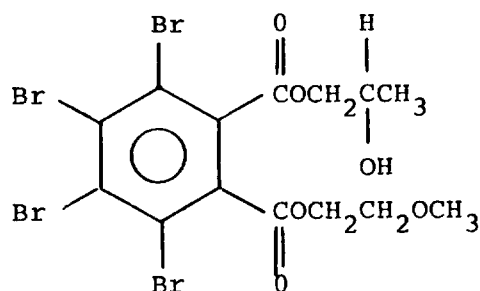
20

This compound was prepared by the procedure in Example 29 except that 2-methoxyethanol is used in place of methanol. Product is viscous liquid. Calcd. % Br, 53.6. Found % Br, 52.0. Analytical data is consistent with the assigned

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structure.

5



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EXAMPLE 32

15

This compound was prepared by the procedure outlined in Example 29 except that methoxycarbowax 350 was used in place of methanol and epoxybutane in place of propylene oxide. Product is a viscous liquid. Calcd. % Br, 36.5. Found % Br, 37.2. Analytical data is consistent with the assigned structure.

20

BrC1C(Br)C(Br)C(Br)C1C(=O)CC(O)CC
BrC1C(Br)C(Br)C(Br)C1C(=O)OCCOCCOCCOCCOCCOCCOCC

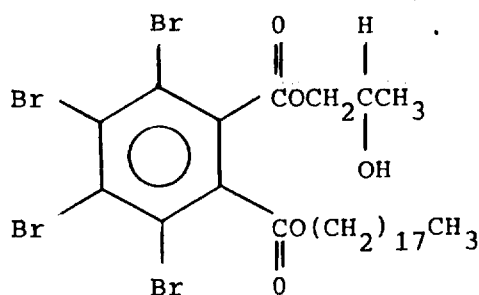
EXAMPLE 33

15 Analytical data is consistent with the assigned
 structure.

BrC1C(Br)C(Br)C(Br)C1C(=O)CC(C)OCC(=O)CC(C)CC

EXAMPLE 34

This compound was prepared by the procedure described in Example 29 except that stearyl alcohol was used in place of methanol. Product is a viscous liquid. Calcd. % Br, 41.0. Found % Br, 43.0. Analytical data is consistent with the assigned structure.

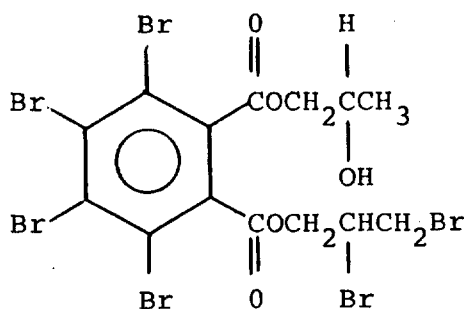


EXAMPLE 35

This compound was prepared by the procedure described in Example 29 except that 2,3-dibromopropanol-1 was used in place of methanol. Product

is a viscous liquid. Calcd. % Br, 64.8. Found
% Br, 61.9. Analytical data is consistent with
the assigned structure.

5

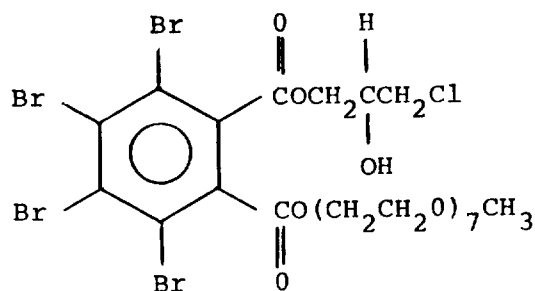


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EXAMPLE 36

This compound was prepared by the procedure
outlined in Example 29 except that epichlorohydrin
was used in place of propylene oxide. Calcd. % Br,
35.7. Found % 35.4. Analytical data is consistent
with the assigned structure.

20



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EXAMPLE 37

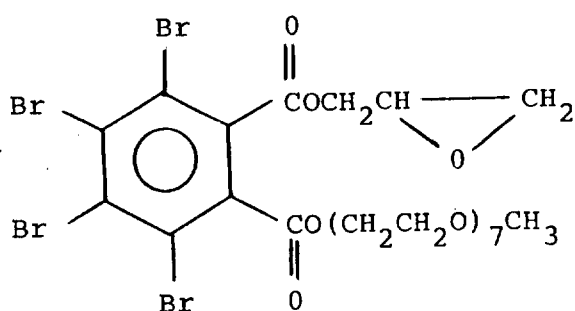
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To a solution of methoxycarbowax 350 (300.0 g, 0.89 mole) in dry toluene (184 ml) was added sodium methoxide (48.0 g, 0.90 mole) in methanol. The methanol was then distilled off atmospherically. Tetrabromophthalic anhydride was then added (442.2 g, 0.89 mole) along with an additional 50 ml of toluene. The reaction mixture was refluxed for 2 hours and after cooling to room temperature, epichlorohydrin (106.94 g, 1.16 moles) was added. The mixture was refluxed

for 20 hours. After the solvent and excess epi-chlorohydrin were distilled, a viscous dark product was obtained. Calcd. % Br, 37.2. Found % Br, 40.4. Analytical data is consistent with assigned structure.

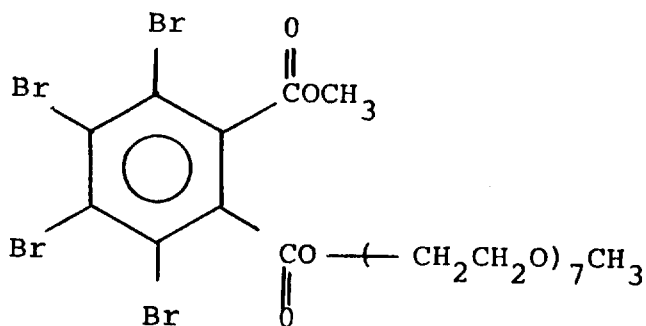


EXAMPLE 38

Methoxycarbowax 350 and toluene were refluxed for 1 hour in order to distill out a small amount of water, Tetrabromophthalic anhydride (1:1 mole ratio with methoxycarbowax 350) and sodium acetate were added and the mixture refluxed for 17 hours.

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After cooling to room temperature, an excess of
diazomethane (prepared from the decomposition of
N-methyl-N-nitroso-p-toluene sulfonamide by
sodium hydroxide) in ethyl ether was added and the
mixture allowed to stand overnight. The excess
diazomethane was decomposed by adding acetic acid
and the solvent removed by distillation. Product
is viscous liquid. Calcd. % Br, 39.2. Found %
Br, 37.4. Analytical data is consistent with the
assigned structure.

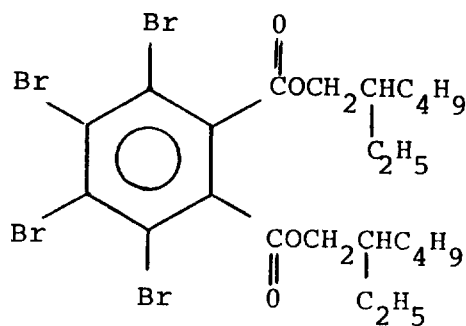


EXAMPLE 39

Di(2-ethylhexyl) tetrabromophthalate was

prepared by the procedure described by Spatz
et. al (I & EC Product Research and Development,
Vol. 8, No. 4, 395 (1969).

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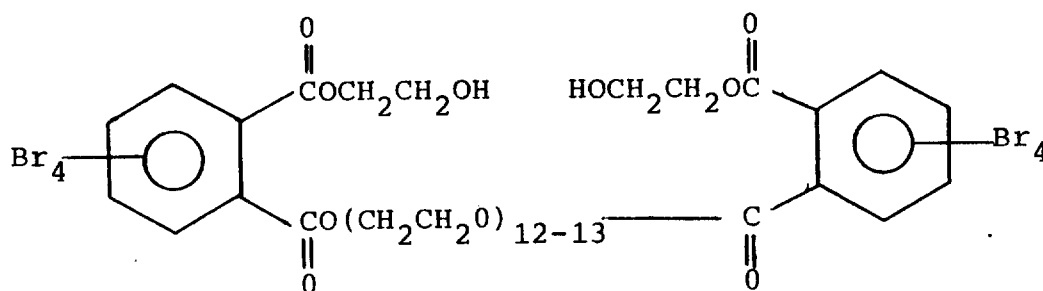


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EXAMPLE 40

Poly(ethylene glycol 600) 835.4 g (1.40
15 moles), tetrabromophthalic anhydride, 1298.4 g
(2.80 moles), potassium acetate, 1.35 g, and
toluene (1000 g) were charged into a one-gallon
glass-lined reactor and heated to 120°C. After
4 hours at this temperature, ethylene oxide,
20 246.68 g (5.60 moles) was pumped into the reactor

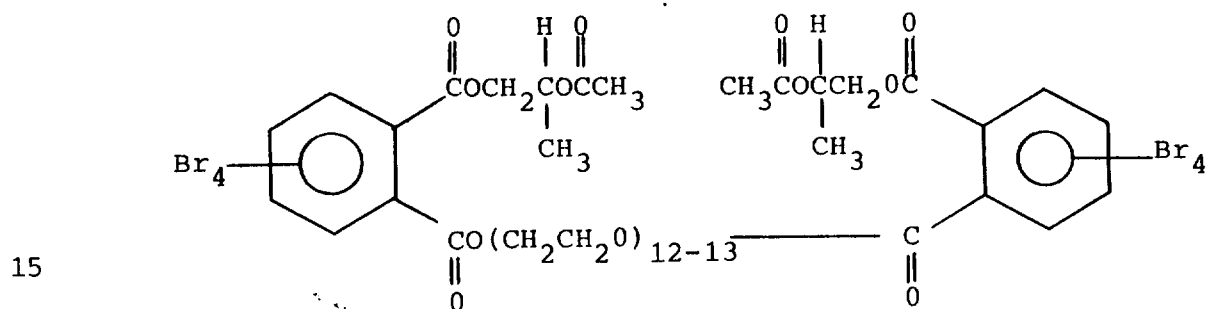
in 3/4 hour while maintaining the temperature at 120°C. After one hour longer of heating, the mixture was cooled to room temperature, the excess ethylene oxide was then vented, and the product collected. After stripping off the toluene, 2250 g of the product was isolated in 99% yield as a viscous liquid. Calcd. % Br, 39.2. Found % Br, 38.8. Analytical data is consistent with the assigned structure.



EXAMPLE 41

To the product of Example 3, 453.8 g (0.27 mole), acetic anhydride, 83.4 g (0.82 mole),

potassium acetate, 1.0 g, and toluene, 400 ml,
 were refluxed for 8 hours. After cooling to
 room temperature, the reaction mixture was
 transferred to a separatory funnel and extracted
 5 first with 100 ml of a 16% potassium bicarbonate
 solution and then with 100 ml of water. After
 distilling off the solvent, 335.0 g (54% yield)
 of product was obtained as a viscous liquid.
 Calc. % Br, 36.8. Found % Br, 32.9. Analytical
 10 data is consistent with the assigned structure.

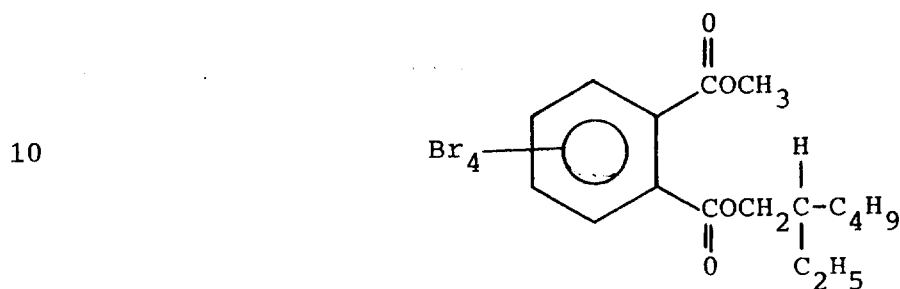


EXAMPLE 42

20 Tetrabromophthalic anhydride, 231.9 g

(0.50 mole), 2-ethylhexanol, 130.2 g (1.0 mole), and potassium acetate 0.24 g were heated to and kept at 120°C for 4 hours. The mixture was cooled to 60°C and potassium carbonate, 35.9 g (0.26 mole), was added. Reheated mixture to 80°C and kept it at this temperature for 2 hours. Cooled mixture to 60°C and added triethylamine, 14.2 g (0.14 mole). Reheated mixture to 70°C and added methyl iodide, 113.6 g (0.8 mole) in 20 minutes. Heated mixture to 70-75°C and kept it at this temperature for 2-1/2 hours. Cooled mixture to room temperature and filtered it in order to remove by-product potassium iodide. The filtrate was distilled to remove toluene and 290 g of crude product was collected as a pale yellow liquid. Extracted this product with 3 times 100 ml of a 6.5% potassium carbonate solution followed by 2 times 100 ml of water and once with a 30% sodium chloride solution. Dried the organic phase over anhydrous magnesium sulfate overnight.

Filtered off magnesium sulfate and after removing the solvent from filtrate by distillation, 204 g of product was obtained in 67% yield as a pale yellow liquid. Calcd. % Br, 52.6. Found % Br, 52.2. Analytical data is consistent with the assigned structure.



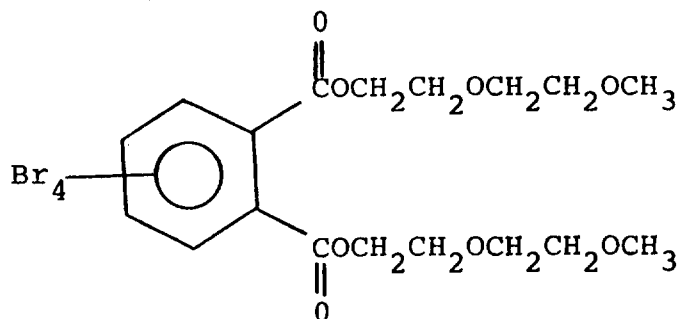
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EXAMPLE 43

Tetrabromophthalic anhydride, 231.9 g (0.5 mole), 2-(2-methoxyethoxy)-ethanol, 360.5 g (3.0 moles), stannous oxalate, 2.32 g, and xylene, 200 ml, were refluxed (temp. 160°C) for 18 hours during which time, theory water was collected.

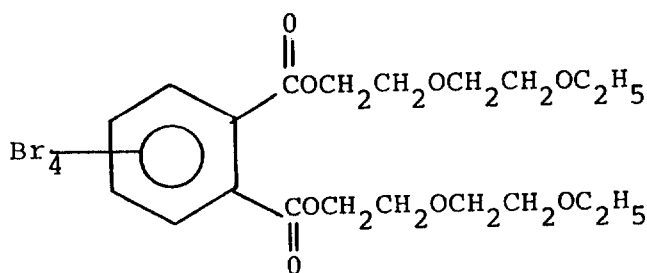
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The xylene and excess 2-(2-methoxyethoxy)-ethanol were distilled under reduced pressure to give 332 g of crude product as a wet white solid. Redissolved 256 g of this material in toluene (1000 ml) and extracted it with 3 times 200 ml of a 7.5% potassium bicarbonate solution followed by one extraction with 200 ml of water. Dried the organic phase with anhydrous magnesium sulfate overnight. After removing the magnesium sulfate by filtration, toluene was removed by distillation to give 45 g of a yellow liquid product. Overall yield is 17%. Calcd. % Br, 46.6. Found % Br, 45.7. Analytical data is consistent with the assigned structure.



EXAMPLE 44

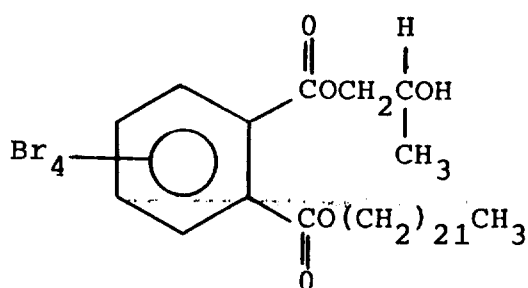
This compound was prepared by the procedure outlined in Example 43 except using 2-(2-ethoxyethoxy)-ethanol.



EXAMPLE 45

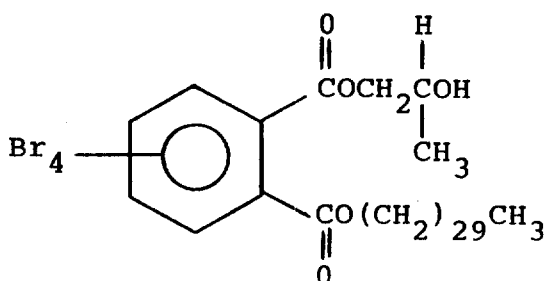
This compound was prepared by the procedure outlined in Example 1 except that docosyl alcohol (behenyl alcohol) was used in place of poly(ethylene glycol 600) and propylene oxide in place of ethylene oxide. Product is a viscous liquid. Calcd. % Br, 37.7. Found % Br, 36.5. Analytical data is consistent with the assigned

structure.



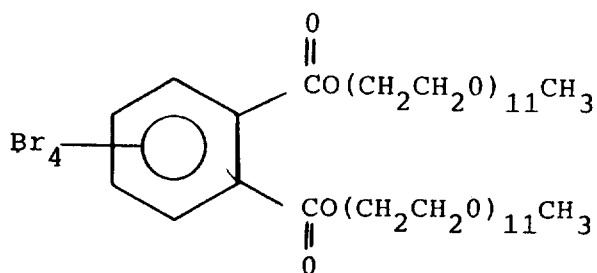
10 EXAMPLE 46

This compound was prepared by the procedure outlined in Example 1 except that tricontyl alcohol was used in place of poly(ethylene glycol 600) and propylene oxide in place of ethylene oxide. Product is a viscous liquid.



EXAMPLE 47

This compound was prepared by the procedure outlined in Example 4 except that methoxycarbowax 350 was used in place of 2-(2-methoxyethoxy)-ethanol.



EXAMPLES 48-58

Compositions With ABS Resins

In the following examples, the flame retardancy of the compounds of this invention are demonstrated with respect to ABS resins. The compositions were prepared by mixing together the

flame retardants, antimony oxide, and ABS on a roller until the compounds were blended thoroughly. The compounds were pelletized at 230-245°C and then injection molded into test specimens at 230°C. The UL-94 vertical burn test was run and compared to a control consisting of ABS itself.

ABS = Acrylonitrile-styrene-butadiene terpolymer

DTBPE = 1,2-bis(2,4,6-tribromophenoxy)-ethane
(70% Bromine)

DOTBP = Dioctyl tetrabromophthalate (45% Bromine)

AO = Antimony Oxide

TABLE I (A)

<u>Example No.</u>	<u>48 (b)</u>	<u>49 (c)</u>	<u>50</u>	<u>51</u>
ABS (a)	100	100	100	100
DTBPE	-	22	11	5.5
DOTBP	-	-	17	25.7
AO	-	4	4	4
UL-94 ^(a) 0.125"	Failed	V-0	V-0	V-0
^(a) 0.062"	Failed	V-1	V-1	V-1

(a) Cyclolac ^(R) T, a product of Borg-Warner Co., U.S.A.

(b) control (100% ABS)

(c) comparison (no tetrahalophthalate ester)

The above clearly demonstrates the flame retardancy of the ABS compositions of this invention relative to the control. These compositions have at least equivalent flame retardancy to the conventional flame retardant used in ABS (DTBPE).

EXAMPLES 52-55

Impact strength of the various materials were determined according to ASTM D256.

TABLE II(A)

<u>Example No.</u>	<u>52(b)</u>	<u>53(c)</u>	<u>54</u>	<u>55</u>
ABS(a)	100	100	100	100
DTBPE	-	22	11	5.5
DOTBP	-	-	17	25.7
AO	-	4	4	4
NOTCHED IZOD IMPACT	3.34	1.26	1.98	1.66

(a) Cycolac[®] T, a product of Borg-Warner Co., U.S.A.

(b) control (100% ABS)

(c) comparison (no tetrahalophthalate ester)

As can be seen from the data above, the conventional flame retardant, DTBPE, greatly reduces the impact strength of ABS compared to those examples where a portion of the DTBPE is replaced by the ABS-containing flame retardant compositions of this invention.

EXAMPLES 56-58

Heat Deflection Temperature (HDT) of the various materials were determined according to ASTM D648.

TABLE III (A)

<u>Example No.</u>	<u>56(b)</u>	<u>57(c)</u>	<u>58</u>
ABS(a)	100	100	100
DTBPE	-	22	11
DOTBP	-	-	17
AO	-	4	4

HEAT DEFLECTION TEMP. (HDT)

@ 264 psi (°F) 182 167 166

-
- (a) Cycolac [®] T, a product of Borg-Warner Co., U.S.A.
 (b) control (100% ABS)
 (c) comparison (no tetrahalophthalate ester)

The data above shows that there is negligible charge in HDT when a portion of the conventional flame retardant, DTBPE, is replaced by the esters disclosed in this invention.

5

EXAMPLES 59-64

Compositions With Polystyrene Resins

In the following examples, the flame retardancy of the compositions of this invention are demonstrated. The compositions were prepared by mixing together the flame retardants, antimony oxide, and high impact polystyrene on a roller until the compounds were blended thoroughly. The compounds were pelletized at 200-260°C. and then injection molded into test specimens at 230°C. The UL-94 vertical burn test was run and compared to a control consisting of the impact polystyrene itself.

HIPS = High Impact Polystyrene
DBDPO = Decabromodiphenyl Oxide (83% Bromine)
DOTBP = Dioctyl Tetrabromophthalate (45% Bromine)
AO = Antimony Oxide

TABLE I (B)

Example No.	59(b)	60(c)	61	62	63	64
	Percentage Composition					
HIPS(a)	100	84	81.5	73.9	83	80.8
DBDPO	-	12	9	-	9	-
DOTBP	-	-	5.5	22.1	4.3	16.4
AO	-	4	4	4	3.7	2.8
UL-94 @ 0.125"	Failed	V-0	V-0	V-0	V-0	V-0
② 0.062	Failed	V-2	V-0	V-0	V-0	V-2

(a) Polysar [®] 525, a product of Polysar, Inc., U.S.A.

(b) control (100% polystyrene)

(c) comparison (no tetrahydrophthalate ester)

5 The above results clearly demonstrate the superior flame retardancy of the styrene-containing flame retardant composition of this invention over the conventional flame retardant used in polystyrene (DBDPO).

10 Examples 60 through 62 are all run at equal bromine levels. Partial or total replacement of the conventional flame retardant (DBDPO) with the esters disclosed in this invention improves the flame retardancy of the polystyrene as can be seen by the UL-94 results for the 0.062" specimens. Examples 63 and 64 clearly demonstrate that the total bromine levels can be reduced when the compositions of this in-
15 vention are used and still yield comparable or better flame retardancy.

EXAMPLES 65-70

20 Impact strength of the various materials were determined according to ASTM D2463.

TABLE II(B)

Example No.	65(b)	66(c)	67	68	69	70
HIPS	100	84	81.5	76.4	73.9	80.8
DBDPO	-	12	9	3	-	-
DOTBP	-	-	5.5	16.6	22.1	16.4
AO	-	4	4	4	4	2.8
Gardner Impact (in-lb/mil)	0.096	0.067	0.070	0.084	0.115	0.095

-
- (a) Polysar [®] 525 from Polysar, Inc.
 (b) control (100% polystyrene)
 (c) comparison (no tetrahalophthalate ester)

As can be seen from the data above, the conventional flame retardant, DBDPO, greatly reduces the impact strength of the polystyrene (see Example 66). The compositions containing the material of the invention clearly improve the impact strength to a point where it is better than the comparison example.

EXAMPLES 71-74

The extrusion rates were measured during pelletization to determine the processing characteristics of the compounds.

TABLE III(B)

Example No.	71(c)	72	73	74
HIPS	84	81.5	79	76.4
DBDPO	12	9	6	3
DOTBP	-	5.5	11	16.6
AO	4	4	4	4
Extruder Flow Rate (lbs/hr)	3.4	3.7	4.2	7.9

-
- (a) Polysar[®] 525, a product of Polysar, Inc., U.S.A.
(c) comparison (no tetrahalophthalate ester)

5 The data above clearly demonstrates the
improved processability of the styrene-containing
flame retardant of this invention.

EXAMPLES 75-79

10 Compositions With Polycarbonate Resins

 In the following examples, the flame
retardancy of the compositions of this invention
are demonstrated with respect to polycarbonate
resins. The compositions were prepared by mixing
15 together the flame retardants, antimony oxide,
and polycarbonate resin on a roller until the
compounds were blended thoroughly. The compounds
were pelletized at 160-305°C and then injection
molded into test specimens at 271°C. The UL-94
20 vertical burn test was run and compared to a

control consisting of the polycarbonate resin
itself. The following tests were performed on
the various materials according to the appropriate ASTM method.

- 5 1. Limited Oxygen Index (LOI) - ASTM D-2863
 2. Melt Flow - ASTM D-1238
 3. Tensile Strength - ASTM D-638

 PC = Polycarbonate polymer
10 BPC = Brominated Polycarbonate Oligomer
 (58% Bromine)
 DOTBP = Dioctyl Tetrabromophthalate
 (45% Bromine)

15

20

TABLE I (C)

Example no.	75 (b)	76 (c)	77	78	79
PC (a)	100.0	87.5	86.6	84.9	84.0
BPC	-	12.5	9.4	3.1	-
DOTBP	-	-	4.0	12.0	16.0
LOI	28	39	37	37	37
Melt Flow (g/10 min)	26.8	19.1	37.5	> 100	> 100
Tensile Strength at Yield (PSI) (d)	9210	10220	10010	10100	10300
% Elongation at Yield	17.9	18.8	17.4	14.3	15.9

-
- 5 (a) "Lexan" 141, a product of General Electric, U.S.A.
(b) control (100% polycarbonate)
(c) comparison (no tetrahalophthalate ester)
(d) PSI = pounds per square inch. 1 PSI = .0145 g/cm²

10 The above clearly demonstrates the significant
improvement in flame retardancy of the polycarbonate
resin containing compositions of this invention
relative to the control. These polycarbonate
resin containing compositions have at least
comparable flame retardancy to the conventional
flame retardant, BPC, used in polycarbonate.

15 Examples 76-79 are all run at equal bromine
levels. Partial or total replacement of the
conventional flame retardant, BPC, with the esters
disclosed in this invention results in greatly
enhanced flow characteristics as shown by the
improved melt flow properties measured according
20 to ASTM D-1238.

The polycarbonate resin containing compositions of this invention show improved tensile properties when compared to the control, and comparable to that of the conventional flame retardant, BPC. Furthermore, the polycarbonate resin containing compositions of this invention maintain percent elongation.

The data above clearly demonstrates the improved processability of the polycarbonate resin containing compositions of this invention.

EXAMPLES 80-86

Compositions With PBT Resins

In the following examples, the flame retardancy of the compounds of this invention are demonstrated. The compositions were prepared by mixing together the flame retardants, antimony oxide, and polybutylene terephthalate (PBT) on a roller until the compounds were blended thoroughly. The compounds were pelletized at 150-216°C and then injection molded into test

specimens at 235°C. The UL-94 vertical burn test was run and compared to a control consisting of PBT itself. Melt flow of the various materials were determined according to ASTM D-1238.

- 5 PBT = Polybutylene Terephthalate
 BPC = Brominated Polycarbonate Oligomer
 (58% Bromine)
 DOTBP= Dioctyl Tetrabromophthalate (45% Bromine)
 AO = Antimony Oxide

10

TABLE I (D)

<u>Example No.</u>	<u>80(b)</u>	<u>81(c)</u>	<u>82</u>	<u>83</u>
PBT(a)	100.0	85.0	82.8	80.7
BPC	-	15.0	7.5	-
15 DOTBP	-	-	9.7	19.3
Antimony Oxide	-	5.0	5.0	5.0
UL-94 Rating				
@ 0.125"	V-2	V-0	V-0	V-0
20 @ 0.063"	V-2	V-0	V-0	V-0

Melt Flow	27.6	36.2	55.1	72.6
(g/10 min)				

(a) "Celanex" 2000, a product of Hoechst-Celanese
5 Corp., U.S.A.

(b) control (100% polybutylene terephthalate)

(c) comparison (no tetrahalophthalate ester)

10 The above clearly demonstrates the flame
retardancy of the compositions of this invention
relative to the control. These compositions
have at least equivalent flame retardancy to
the BPC conventional flame retardant used in
PBT (Example 81).

15 Examples 81-83 are all run at equal bromine
levels. Partial or total replacement of the
conventional flame retardant (BPC) with the
compositions of this invention results in enhanced
flow characteristics as shown by the improved melt
20 flow properties measured according to ASTM D-1238.

EXAMPLES 84-86

The following tests were performed on the various materials according to the appropriate ASTM method.

- 5 1. Impact Strength - ASTM D-256
 2. Tensile Strength- ASTM D-638
 3. Heat Deflection Temperature (HDT) - ASTM D-648
 4. Melt Flow - ASTM D-1238

10

TABLE II (D)

EXAMPLE NO.	84(b)	85(c)	86
PBT (a)	100	85.0	83.8
BPC	-	15.0	11.3
DOTBP	-	-	4.9
Antimony Oxide	-	5.0	5.0
LOI	25	32	32
UL-94 Rating			
@ 0.125	V-2	V-0	V-0
@ 0.063	V-2	V-0	V-0
Notched Izod	0.45	0.33	0.60
(lbs/inch)			
Tensile Strength	7320	8040	7750
(PSI) (d)			
% Elongation	10.9	10.3	11.8
HDT (°F)/(°C)	127/53	149/65	135/57
Melt Flow	27.6	36.2	61.9
(g/10 min)			

(a) "Celanex" 2000, a product of Hoechst-Celanese Corp., U.S.A.

(b) control (100% polybutylene terephthalate)

5 (c) comparison (no tetrahalophthalate ester)

(d) PSI = pounds per inch. 1 PSI = .0145 g/cm²

As can be seen from the data above, polybutylene terephthalate resin compositions containing the flame retardants of this invention greatly improve the impact strength relative to the control (Example 84) and the BPC conventional flame retardant, (Example 85) used in PBT while maintaining both tensile strength and percent elongation properties.

10

15

In addition, the flame retardants of this invention significantly improve the heat distortion temperature (HDT) and flow properties relative to the control.

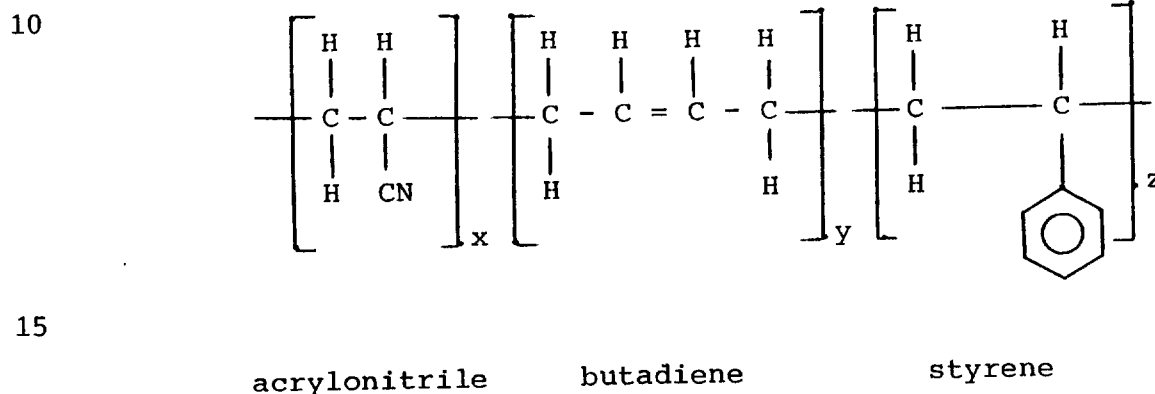
20 The data above clearly demonstrates the improved processability of the polybutylene terephthalate containing compositions according to this invention.

WE CLAIM:

1. A flame retardant plastic composition with improved flow characteristics comprising the mixture of:

(I) a resin which is selected from the group consisting of:

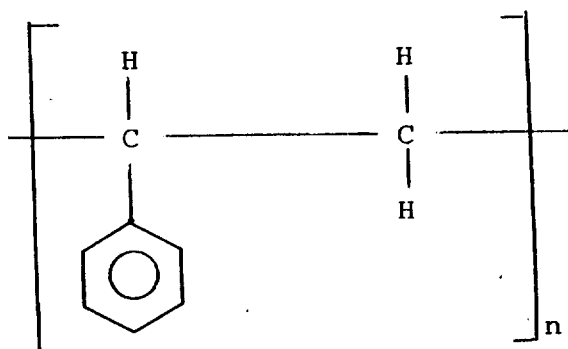
(A) Acrylonitrile-Butadiene-Styrene resin of the formula



wherein x, y and z may independently vary from 10 to 1,500;

(B) Polystyrene resin and is one of:

(a) a homopolymer of styrene having
the following repeatable unit:



wherein n is within the range of
greater than 1 to about 3,000;

(b) a homopolymer of styrene as in

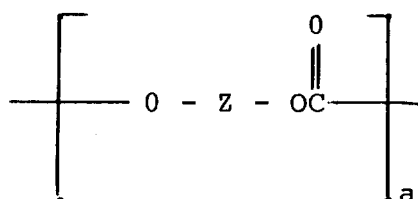
15 (a) modified with rubber in which
the rubber is dispersed as discrete
particles into a matrix of said
homopolymer and the weight ratio of
rubber to homopolymer is within the
20 range of from about 2:98 to about

5

25:75; or (c) a copolymer of butadiene and styrene in which the weight ratio of butadiene to styrene is within the range of about 2:98 to about 25:75; or (d) blends of (a) and (b);

(c) Polycarbonate resin which has repeated structural units of the formula:

10

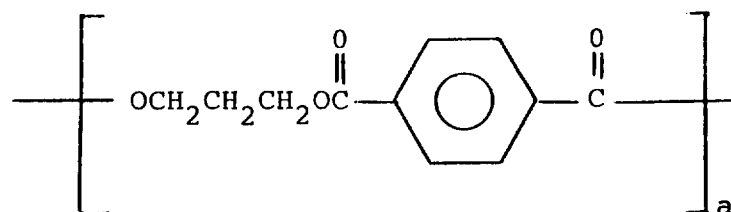


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wherein a is greater than 1 and Z is a divalent aromatic radical of a dihydric phenol; and

(D) Polybutylene Terephthalate resin and has repeated structural units of the formula:

20



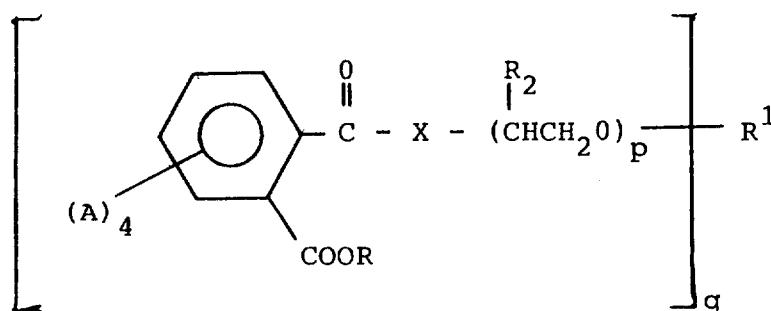
5

wherein $a > a$; and

(II) a flame retarding effective amount of a tetrahalophthalate ester flame retardant processing aid and has the formula:

10

15



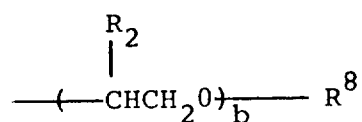
wherein:

20

(a) R is selected from the group

consisting of hydrogen, an
alkyl or substituted alkyl
of 1 to 9 carbons and

5

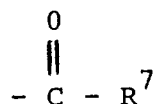


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where R⁸ is an alkyl or substituted alkyl of 1 to 18 carbons,
and b is 1 to 50;

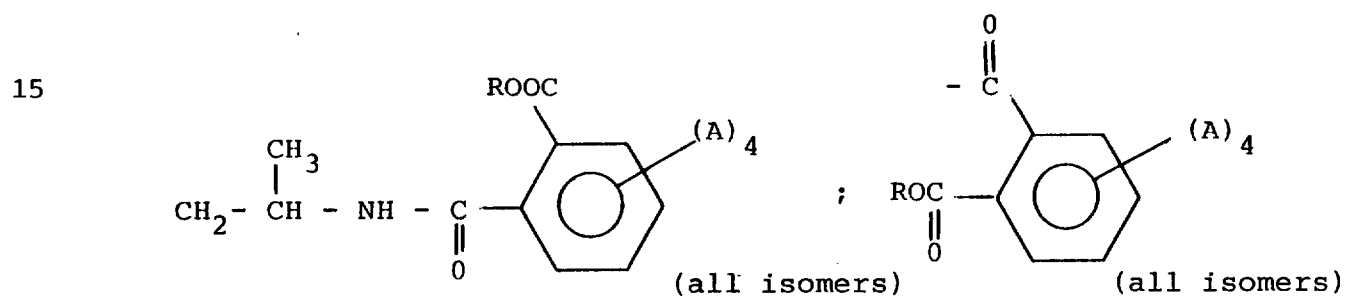
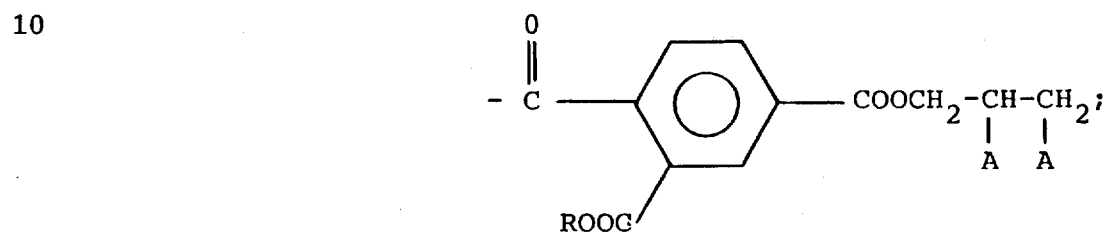
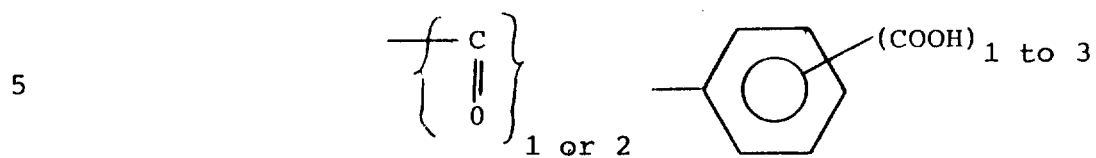
- (b) R¹ is selected from the group
consisting of an alkyl or
substituted alkyl of 1 to 9
carbons, alkenyl or substituted
alkenyl of 1 to 22 carbons;

15

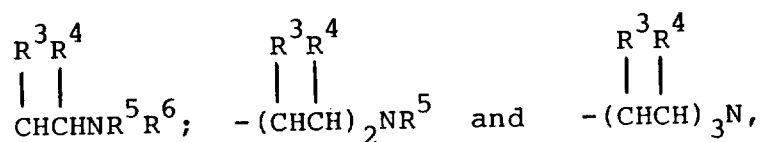


20

where R⁷ is an alkyl of 1 to
18 carbons;



20



5

with the proviso that the valence
of R^1 is equal to q ;

(c) R^2 is independently selected from
the class consisting of H and CH_3 -;

10

(d) R^3 , R^4 , R^5 and R^6 are independently
selected from the class consisting
of H and an alkyl of 1 to 18
carbons;

(e) p is an integer of 0 to 50;

(f) q is an integer of 1 to 6;

15

(g) X is selected from 0 to NH, and

(h) A is selected from Cl or Br.

20

2. A method for imparting flame retardant
and improved flow characteristics to a resin
according to claim 1 comprising mixing with said

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resin a flame retardant effective amount of at least one tetrahalophthalate ester flame retardant aid according to claim 1.

5 / 3. A method for manufacturing a flame retardant resin with improved flow characteristics comprising mixing a resin according to claim 1 and a flame retarding effective amount of at least one tetrahalophthalate ester flame retardant aid
10 according to claim 1.

 / 4. A composition according to claim 1 wherein p is zero, q is one and X is oxygen.

15 / 5. A composition according to claim 6 wherein R and R¹ are alkyl groups and A is Br.

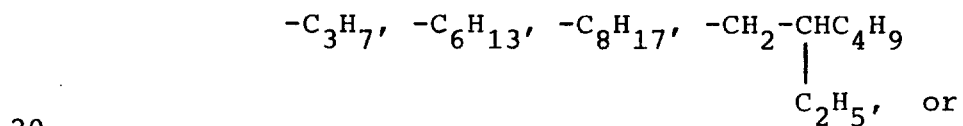
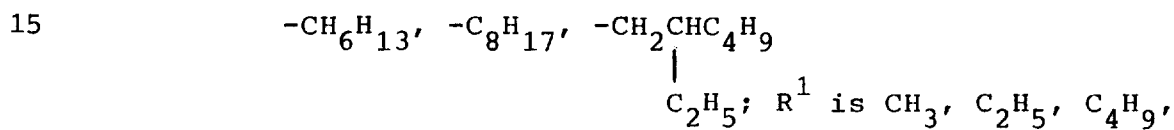
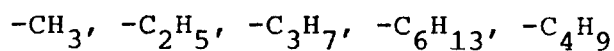
 6. A composition according to claim 5 wherein the ester is di-2-ethylhexyl tetrabromophthalate.

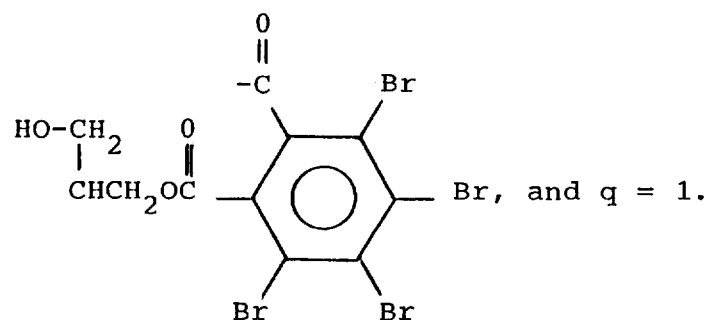
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7. A composition according to claim 1 wherein the weight ratio of (I) to (II) is within the range of 100:1 to 2:1.

5 8. A composition according to claim 1 wherein
R is an alkyl as substituted alkyl of 1 to 9
carbons, A is Br, X is oxygen, p is 0 to 20,
and q is 1 to 6.

10 9. A composition according to claim 1 wherein
R is selected from among

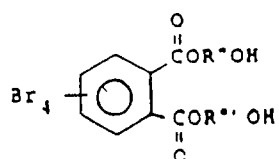
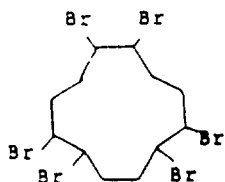
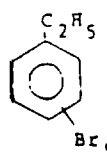
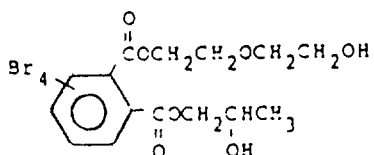
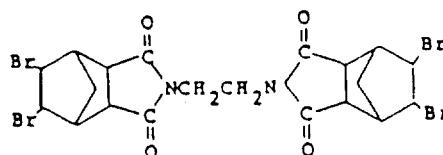
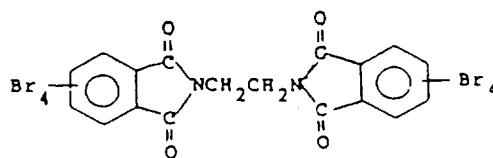




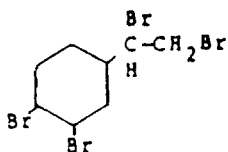
10 10. A composition according to claim 1 wherein
 (II) includes additional brominated or chlorinated
 flame retardants or mixtures thereof other than
 said ester.

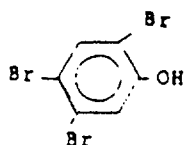
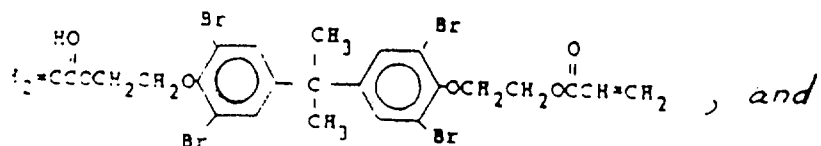
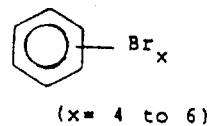
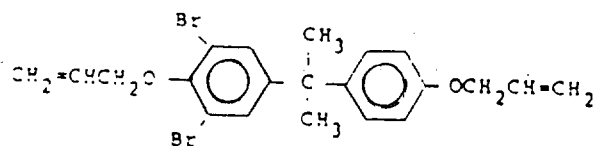
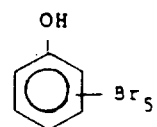
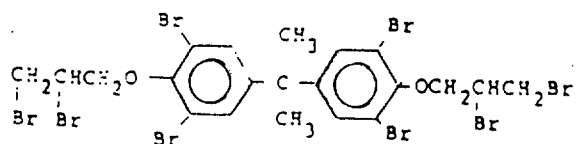
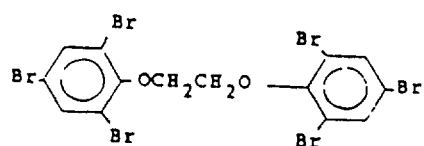
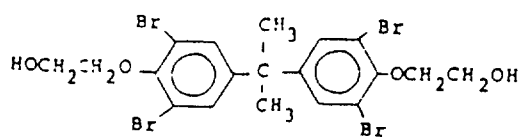
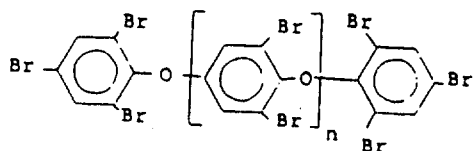
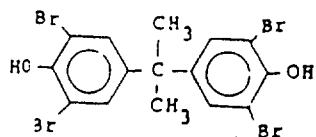
15 11. A composition according to claim 10
 wherein said additional flame retardants are
 selected from the group consisting essentially of

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where R' and R'' are
alkylene or substituted alkylene





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12. A composition according to claim 1 wherein
the resin is acrylonitrile-butadiene-styrene and
a portion or all of acrylic and styrenic monomers
comprising the resin include methacrylonitrile or
5 α -methylstyrene.

13. A composition according to claim 12 where
the resin comprises monomeric units of a vinyl
aromatic monomer, a vinyl nitrile monomer, and a
10 butadiene monomer.

14. A composition according to claim 1 wherein
the Polystyrene resin is (B) (a) and is in the form
of a foam.

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