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(54) Title: FLAME RETARDANT POLYCARBONATE COMPOSITIONS

(57) Abstract

Flame retardant polycarbonate compositions are disclosed which are obtained from polymers derived from non-polycyclic, sulfur-free diphenols and polymers derived from sulfur-containing diphenols.

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Description

Flame Retardant Polycarbonate Compositions

This invention relates to thermoplastic, amorphous, halogen-free aromatic, high molecular weight polycarbonate compositions having improved flame retardance.

BACKGROUND OF THE INVENTION

The increasing concern for safety has resulted in increased efforts towards providing safer materials for commercial and household use. One particular area of need is that of providing flame retardant plastic products, many of which are now required to meet certain flame retardant criteria established by local and federal governments as well as by the manufacturers of such products. One particular set of conditions commonly accepted and used as a standard for flame retardancy is that which is set forth in Underwriters' Laboratories, Inc. Bulletin 94 which proscribes certain conditions by which materials are rated for self-extinguishing characteristics.

It is known that various halogen-containing, flame retardant additives can be employed to render plastic products self-extinguishing or flame retardant. Such flame retardant additives are typically employed in amounts sufficient to be effective for their intended purpose; generally, on the order of about 5-20% by weight based upon the weight of the plastic composition. In many instances, use of these flame retardants in such amounts can have a degrading affect upon the plastic compositions to be rendered flame retardant often resulting in the deterioration of valuable physical properties of the base polymer. This is particularly so when known flame retardant additives are employed with polycarbonate resins since many of these additives have a degrading affect upon the base polymer typically resulting in discoloration and a loss of impact strength.

It is also known that blends and/or copolymers of halogen-containing copolycarbonates and aromatic thiodiphenols can be employed to obtain flame retardant compositions. For example, U.S. Patent 4,043,980 discloses polycarbonate compositions obtained as the reaction product of an aromatic diol, a halogenated phenol, and a carbonic acid coreacted with an aromatic thiodiphenol (TDP), which compositions exhibit flame retardancy stated to be the result of the synergism between the sulfur and the halogen present in the composition. It is also disclosed that such compositions overcome the detrimental critical thickness effect; i.e., that thickness at which notched Izod impact values of a test sample began to decrease, due to the presence of sulfur in the compositions.

In U.S. Patent 4,174,359, flame retardant polycarbonate compositions are disclosed which are obtained as blends of a polycarbonate - TDP copolymer and a halogen-containing compound. The compositions can optionally include small amounts of a sulfonic or carboxylic acid salt which are preferably perfluorinated.

Other sulfur-containing polycarbonate compositions are also known such as crystalline copolycarbonates obtained as the reaction of polycarbonate and TDP as disclosed in "Polycarbonates and Mixed Polycarbonates based on Bis(4-hydroxyphenyl)sulfide", O.V. Smirnova, G.S. Kolesnikov, A.K. Mikitaeo and T.G. Krichevskaya (Mosk. Khim-Teckhnol. Inst. im Mendeleeva, Moscow), Vysokomol Soldin, Ser. 4 10(1), 96 101 (1968) (Russ), also reported in "Chem. Abstracts:, 68, 1968.

In addition, U.S. Patent 3,398,212 discloses copolymers and blends of copolycarbonates and copolyesters prepared from halogenated or non-halogenated polycyclic bisphenols and TDP.

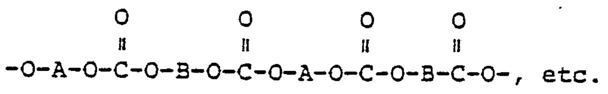
Further, in an article entitled "Linear Aromatic Polyesters of Carbonic Acid", H. Schnell (Ind. Chem. Eng., 1959) there is disclosed crystallizable polycarbonates which can contain TDP.

DESCRIPTION OF THE INVENTION

It has now been found that the flammability of halogen-free, conventional, aromatic polycarbonate compositions can be dramatically improved by the incorporation therein of sulfur-containing polycarbonates derived from sulfur-containing diphenols. The effect is truly remarkable in that high degrees of flame retardancy are achieved without the presence of any halogen additives and/or halogen-containing polycarbonates.

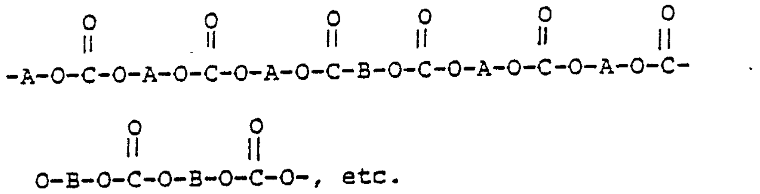
The sulfur-containing aromatic polycarbonates can be present as copolycarbonates derived from mixtures of non-polycyclic, sulfur-free and sulfur-containing diphenols or as blends of conventional polycarbonates and sulfur-containing polycarbonates. The term "conventional" as used throughout this application is intended to encompass and should be understood as encompassing polycarbonates derived from diphenols that are non-polycyclic and that are free of sulfur and halogen substituents in their molecular structure.

The flame retardant polycarbonate compositions of the invention comprise the sulfur-free and sulfur-containing diphenols either as a chemical mixture or a physical mixture, or both. When present as a chemical mixture, the sulfur-free polycarbonate and the sulfur-containing polycarbonate are linked together by chemical bonds, such as in copolycarbonates. Thus, copolycarbonates of two, or more, components can be coreacted to form alternating or random or block copolycarbonates as well as chemical mixtures thereof. Represented symbolically by A and B for the two diphenol-derived moieties, an alternating copolycarbonate structure would be as follows:



$$-O-A-O-\overset{\overset{O}{\|}}{C}-O-B-O-\overset{\overset{O}{\|}}{C}-O-A-O-\overset{\overset{O}{\|}}{C}-O-B-\overset{\overset{O}{\|}}{C}-O-, \text{ etc.} \qquad \text{I.}$$

while a random copolycarbonate would have the structure:

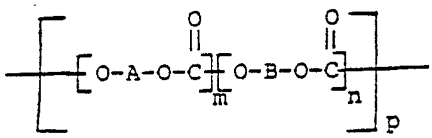


$$-A-O-\overset{\overset{O}{\|}}{C}-O-A-O-\overset{\overset{O}{\|}}{C}-O-A-O-\overset{\overset{O}{\|}}{C}-B-O-\overset{\overset{O}{\|}}{C}-O-A-O-\overset{\overset{O}{\|}}{C}-O-A-O-\overset{\overset{O}{\|}}{C}-$$

$$O-B-O-\overset{\overset{O}{\|}}{C}-O-B-O-\overset{\overset{O}{\|}}{C}-O-\text{, etc.}$$

II.

and a block copolycarbonate would have the structure:



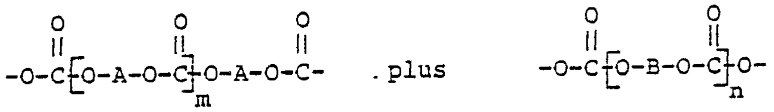
$$-\left[\left[O-A-O-\overset{\overset{O}{\|}}{C}\right]_m\left[O-B-O-\overset{\overset{O}{\|}}{C}\right]_n\right]_p-$$

III.

wherein m and n are greater than 1 and p is at least 1.

Chemical mixtures of such copolycarbonates would be represented by structures in which the structures shown in formulae I and/or II and/or III are joined together by chemical bonds.

The non-polycyclic, sulfur-free polycarbonate and the sulfur-containing polycarbonate can also be present as a physical mixture or blend, of two or more components wherein no chemical interaction occurs and, thus, no chemical bonds are present linking the components together. Represented symbolically, a physical mixture of the two polycarbonates, in its simplest form, would be as shown below:



$$-O-\overset{\overset{O}{\|}}{C}\left[O-A-O-\overset{\overset{O}{\|}}{C}\right]_m O-A-O-\overset{\overset{O}{\|}}{C}- \quad \text{plus} \quad -O-\overset{\overset{O}{\|}}{C}\left[O-B-O-\overset{\overset{O}{\|}}{C}\right]_n O-$$

IV.

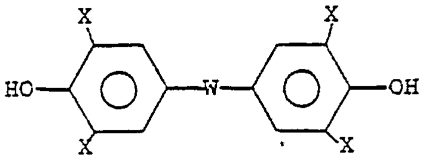
IVa IVb

wherein m and n have the same value as above, or as physical mixtures of IVa with I and/or II and/or III, or as physical mixtures of IVb with I and/or II and/or III, or as physical mixtures of I and II, or I and III, or II and III.

In addition, the polycarbonate composition can comprise both chemical and physical mixtures.

Accordingly, in the practice of this invention, the conventional non-polycyclic aromatic polycarbonates that can be employed are homopolymers and copolymers that can be prepared by reacting a halogen-free and sulfur-free diphenol with a carbonate precursor. Typical of some of the diphenols that can be employed are 2,2-bis (4-hydroxyphenyl)propane, (also known as bisphenol-A or BPA), bis (4-hydroxyphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 4,4-bis(4-hydroxyphenyl)heptane, 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)propane, 3,3-bis(4-hydroxyphenyl)pentane. Other diphenols of the bisphenol type are also available such as are disclosed in U.S. Patents 2,999,835; 3,028,365; and 3,334,154 incorporated herein by reference.

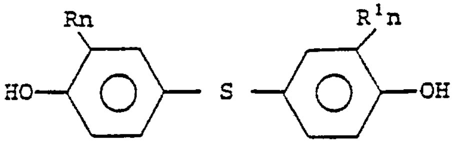
These non-polycyclic, halogen-free and sulfur-free diphenols can be represented by the structural formula:



V.

wherein each X can independently be selected from the group consisting of H or C_1 - C_5 alkyl, and W can be a chemical bond, C_1 - C_8 alkylene, C_2 - C_8 alkylidene, C_5 - C_{12} cycloalkylene or cycloalkylidene.

The sulfur-containing diphenols from which the sulfur-containing polycarbonates can be obtained, can be represented by the following structural formula:



VI.

wherein R and R^1 can each independently be H or C_1 to C_4 alkyl, and n is 1 or 2. Typical of some of these sulfur-containing diphenols are 4,4'-thiodiphenol; 2-methyl-4,4'-thiodiphenol; 2,2'-dimethyl-4,4'-thiodiphenol, 2,2'-di-tertiary-butyl-4,4'-thiodiphenol, and the like, all of which are collectively referred to as "thiodiphenol" or "TDP". Such thiodiphenols can be prepared by known methods such as that disclosed in U.S. Patent 3,931,335 incorporated herein by reference.

It is, of course, possible to employ two or more different diphenols in either or both the sulfur-free and sulfur-containing components or a copolymer of a diphenol with a glycol or with hydroxy or acid terminated polyester, or with a dibasic acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in the preparation of the aromatic carbonate polymers of this invention. Also, blends of any of the above materials can be employed to provide the aromatic polycarbonate.

The carbonate precursor can be either a carbonyl halide, a carbonate ester or a haloformate. The carbonyl halides which can be employed are carbonyl bromide, carbonyl chloride and mixtures thereof. Typical of the carbonate esters which can be employed are diphenyl carbonate, di-(halophenyl)carbonates such as di-(chlorophenyl) carbonate, di-(bromophenyl) carbonate, di-(trichlorophenyl) carbonate, di-(tribromophenyl) carbonate, etc., di-(alkylphenyl) carbonates such as di(tolyl) carbonate, etc., di-(naphthyl)carbonate, di-(chloronaphthyl)carbonate, phenyl tolyl carbonate, chlorophenyl chloronaphthyl carbonate, etc., or mixtures thereof. The haloformates which can be used include bis-haloformates of the diphenols employed, including both the sulfur-free and sulfur-containing bisphenols, such as BPA-bis(chloroformate) and thiodiphenol bis-(chloroformate) and their congeners. While other carbonate precursors will occur to those skilled in the art, carbonyl chloride, also known as phosgene, is preferred.

The aromatic carbonate polymers of this invention can be prepared by employing a molecular weight regulator, an acid acceptor and a catalyst. The molecular weight regulators which can be employed include monohydric phenols such as phenol, chroman-I, paratertiarybutylphenol, parabromophenol, and the like. Preferably, phenol is employed as the molecular weight regulator.

The acid acceptor can be either an organic or an inorganic acid acceptor. A suitable organic acid acceptor is a tertiary amine and includes such materials as pyridine, triethylamine, dimethylaniline, tributylamine, etc. The inorganic acid acceptor can be one which can be either a hydroxide, a carbonate, a bicarbonate, or a phosphate of an alkali or alkaline earth metal.

The catalysts which can be employed are any of the catalysts that aid the polymerization of the diphenol such as bisphenol-A with phosgene. Suitable catalysts include tertiary amines such as for example, triethylamine, tripropylamine, N,N-dimethylaniline, quaternary ammonium compounds such as, for example, tetraethylammonium bromide, cetyl triethylammonium bromide, tetra-n-heptylammonium iodide, tetra-n-propylammonium bromide, tetramethylammonium chloride, tetramethylammonium hydroxide, tetra-n-butylammonium iodide, benzyltrimethylammonium chloride and quaternary phosponium compounds such as, for example, n-butyltriphenyl phosphonium bromide and methyltriphenyl phosphonium bromide.

Also, included herein are branched polycarbonates wherein a polyfunctional aromatic compound is reacted with the diphenol and carbonate precursor to provide a thermoplastic randomly branched polycarbonate.

The polyfunctional aromatic compounds contain at least three functional groups which are carboxyl, carboxylic anhydride, haloformyl or mixtures thereof. Examples of the polyfunctional aromatic compounds include trimellitic anhydride, trimellitic acid, trimellityl trichloride, 4-chloroformyl phthalic anhydride, pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, benzophenonetetracarboxylic acid, benzophenonetetracarboxylic anhydride, and the like. The preferred polyfunctional aromatic compounds are trimellitic anhydride or trimellitic acid or their haloformyl derivatives.

Also included herein are blends of a linear polycarbonate and a branched polycarbonate.

In order to impart effective flame-retardancy to the polycarbonate compositions of the invention, the sulfur content thereof should be about 3 - 13, preferably about 5 - 10, weight percent based upon the total weight of the final composition. This amount of sulfur is equivalent to a thiodiphenol content of about 23 - 98 mole percent in the broad range and about 35 - 75 mole percent in the preferred range.

The polycarbonate compositions of the invention exhibit not only excellent flame retardant characteristics, but also exhibit hitherto unknown, felicitious combinations of outstanding properties such as impact strength, especially in thicker sections, and better thermal stability. Therefore, there are included in the test results shown hereinafter not only flame retardancy, but notched Izod impact and thermal gravimetric analyses as well.

PREFERRED EMBODIMENT OF THE INVENTION

The following examples are presented to more fully and clearly illustrate the invention. Although the examples set forth the best mode presently known to practice the invention, they are intended to be and should be considered as being illustrative of, rather than limiting, the invention. In the examples, all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Into a mixture of 2283 grams of pure 4,4'-isopropylidenediphenol (BPA) (mp 156-157°C; 10.0 mole grams), 5700 grams water, 9275 grams methylene chloride, 32.0 grams phenol and 10.0 grams triethylamine were introduced, at ambient temperature, 1180 grams phosgene over a period of 97 minutes while maintaining the pH of the two-phase system at about 11; i.e., pH 10-12.5, by simultaneously adding a 25% aqueous sodium hydroxide solution. At the end of the addition period, the pH of the aqueous phase was 11.7 and the BPA content of this phase was less than 1 part per million (ppm) as determined by ultraviolet analysis.

The methylene chloride phase was separated from the aqueous phase, washed with an excess of dilute (0.01 N) aqueous HCl and then washed three times with deionized water. The polymer was precipiated by steam and dried at 95°C. The resultant, pure BPA-polycarbonate, which had an intrinsic viscosity (IV) in methylene chloride at 25°C of 0.465 dl/g., was fed to an extruder, which extruder was operated at about 550°F, and the extrudate was comminuted into pellets.

The pellets were then injection molded at about 600°F into test bars of about 5 in. by 1/2 in. by about 1/8 in. thick and into stepped test squares of about 2 in. by 2 in. by about 1/8 in. and 1/16 in. thick. The 1/8 in. test bars (5 for each test result shown in the Table) were subjected to the flame-retardancy test procedure set forth in Underwriters' Laboratores, Inc. Bulletin UL-94, Burning Test for Classifying Materials. In accordance with this test procedure, materials that pass the test are rated either V-O, V-I or V-II based on the results of 5 specimens. The criteria for each V (for vertical) rating per UL-94 is briefly as follows:

"V-O": Average flaming and/or glowing after removal of the igniting flame shall not exceed 5 seconds and none of the specimens shall drip flaming particles which ignite absorbent cotton.

"V-I": Average flaming and/or glowing after removal of the igniting flame shall not exceed 25 seconds and the glowing does not travel vertically for more than 1/8" of the specimen after flaming ceases and glowing is incapable of igniting absorbent cotton.

"V-II": Average flaming and/or glowing after removal of the igniting flame shall not exceed 25 seconds and the specimens drip flaming particles which ignite absorbent cotton.

In addition, a test bar which continues to burn for more than 25 seconds after removal of the igniting flame is classified, not by UL-94, but by the standards of the invention, as "burns". Further, UL-94 requires that all test bars in each test group must meet the V-type rating to achieve the particular classification; otherwise, the 5 bars receive the rating of the worst single bar. For example, if one bar is classified as V-II and the other four (4) are classified as V-O, then the rating for all bars is V-II.

Impact measurements by the notched Izod test were determined pursuant to ASTM D-256 on 1/8 in. thick test bars.

Thermal gravimetric measurements were carried out on a Perkin Elmer TGS1 instrument pursuant to ASTM D-1238, condition O.

EXAMPLE 2

The procedure of Example 1 was exactly repeated, except that half of the BPA (1141.5g) was replaced with 1091.5g of 4,4'-thiodiphenol (TDP) (5 moles; i.e., 50 mole % TDP, or about 6.6 wt. % sulfur) and only 19.8g of phenol was employed.

EXAMPLE 3

The procedure of Example 1 was exactly repeated, except that a mixture of 570.7g (2.5 mole) of BPA and 1637.1g of TDP (7.5 moles; i.e., 75 mole % TDP, or 9.8 wt. % sulfur) was used and only 16.9g of phenol was employed.

EXAMPLE 4

Repeating the procedure of Example 1 with a mixture of 1712.5g (7.5 moles) of BPA and 545.7g of TDP (2.5 moles; i.e., 25 mole % TDP, or 3.3 wt. % sulfur) yielded a polycarbonate having an IV of 0.478 dl/g.

The flame retardancy, notched Izod impact and thermal gravimetric results of the copolycarbonate test samples obtained from foregoing Examples are set forth in the Table herein below wherein the sample of Example 1, from which a conventional polycarbonate was obtained, is identified as the "Control".

EXAMPLE 5

The procedure of Example 2 was exactly repeated, except that BPA was replaced with 1342g of 4,4'-cyclohexylidenediphenol. The copolycarbonate obtained was found to be V-O pursuant to UL-94.

EXAMPLE 6

The procedure of Example 2 was repeated except that 1482g of 4,4'-cyclohexlidenebis(2-methylphenol) was employed in place of BPA. The copolycarbonate obtained was found to be V-O pursuant to UL-94.

EXAMPLE 7

A physical mixture consisting of 2560g of the polycarbonate of Example 1 and 2440g of a polycarbonate prepared from TDP and phosgene following the procedure of Example 1 was fed to an extruder operating at about 550^{o}F and the pellets obtained therefrom were molded into test samples as described in Example 1. The clear, colorless test bars obtained had a sulfur content of 6.0 wt. % and were found to be V-O per UL-94.

EXAMPLE 8

Following the procedure of Example 7, additional test bars were obtained from a physical mixture consisting of 128g of the polycarbonate of Example 1 and 2318g of a TDP-polycarbonate. The clear, colorless test bars had a sulfur content of 12.4 wt. % and were found to be V-O per UL-94.

TABLE

TEST SAMPLE FROM EXAMPLE	AMOUNT OF DIPHENOL		MOL. RATIO (BPA:TDP)	SULFUR FOUND (wt %)	INTRINSIC VISCOSITY (dl/g)	N. IZOD (ft. lb.)	THERMAL GRAVIMETRY[a]		UL-94		
	BPA (g)	TDP (g)					5% wt. loss (°C)	50% wt. loss (°C)	Flame-Out Time, (sec.)	Drips (per 5 bars)	Rating
Control	2283	0	1:0	0.0	0.465	16.2	338	380	26	13	Burns
2	1141.5	1091.5	1:1	6.4	0.462	13.4	362	401	3.8	0	V-O
3	570.7	1637.1	1:3	9.7	0.524[b]	13.8	370	414	3.2	0	V-O
4	1712.2	545.7	3:1	3.1	0.478	16.5	350	393	4.6	0	V-O

a) Analyses carried out in air

b) Determined in s-tetrachloroethane instead of methylene chloride

Claims

1. A thermoplastic, amorphous, halogen-free, aromatic, high molecular weight polycarbonate composition derived from a non-polycyclic, sulfur-free diphenol and a sulfur-containing diphenol.

2. The composition of claim 1 wherein the sulfur content thereof is in the range of about 3-13 percent by weight based upon the weight of said composition.

3. The composition of claim 1 wherein said non-polycyclic, sulfur-free diphenol and said sulfur-containing diphenol are polymers present in the form of a physical mixture.

4. The composition of claim 3 wherein one or more of said non-polycyclic, sulfur-free diphenol polymers and one or more of said sulfur-containing diphenol polymers are chemically bonded to each other in the form of block copolymers, random copolymers, alternating copolymers, and mixtures thereof.

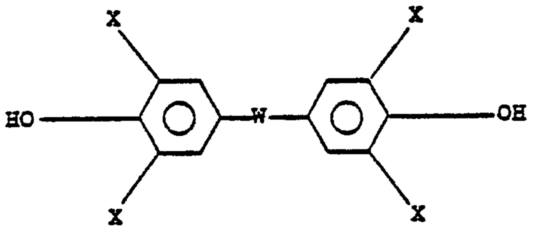
5. The composition of claim 1 wherein said non-polycyclic, sulfur-free diphenol and said sulfur-containing diphenol are polymers chemically bonded to each other.

6. The composition of claim 5 wherein one or more of said non-polycyclic, sulfur-free diphenol polymers and one or more of said sulfur-containing diphenol polymers are chemically bonded to each other in the form of block copolymers, random copolymers, alternating copolymers, and mixtures thereof.

7. The composition of claim 1 wherein said non-polycyclic, sulfur-free diphenol and said sulfur-containing diphenol are polymers present in the form of a blend comprising a physical mixture and moieties chemically bonded to each other.

8. The composition of claim 7 wherein one or more of said non-polycyclic, sulfur-free diphenol polymers and one or more of said sulfur-containing diphenol polymers are chemically bonded to each other in the form of block copolymers, random copolymers, alternating copolymers, and mixtures thereof.

9. The composition of claim 1 wherein said non-polycyclic, sulfur-free diphenol is represented by the structural formula:



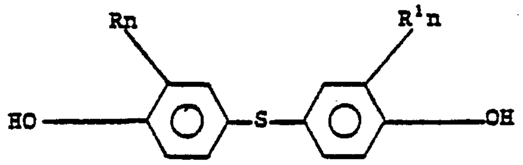
wherein each X can be independently selected from the group consisting of H or C_1 -C_5 alkyl, and W can be a chemical bond, C_1 -C_8 aklyene, C_2 -C_8 alkylidene, C_5 -C_{12} cycloalkylene, or cycloalkylidene.

10. The composition of claim 9 wherein said diphenol is BPA.

11. The composition of claim 9 wherein said diphenol is 4,4' -cyclohexylidenediphenol.

12. The composition of claim 9 wherein said diphenol is 4,4' -cyclohexylidenebis(2-methylphenol).

13. The composition of claim 1 wherein said sulfur-containing diphenol is represented by the structural formula:

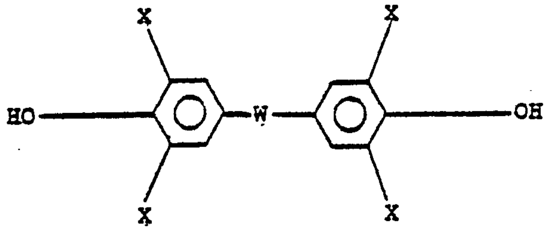


wherein R and R^1 can each independently be H or C_1-C_4 alkyl, and n is 1 or 2.

14. The composition of claim 13 wherein said diphenol is 4,4' -thiodiphenol.

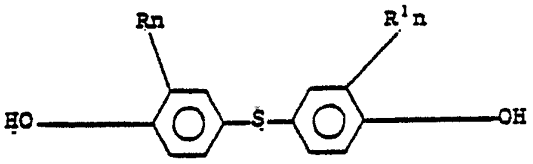
15. A thermoplastic, amorphous, halogen-free, high molecular weight polycarbonate composition derived from:

(a) a non-polycyclic, sulfur-free diphenol represented by the structural formula:



wherein each X can be independently selected from the group consisting of H or C_1-C_6 alkyl, and W can be a chemical bond, C_1-C_6 alkylene, C_2-C_6 alkylidene, C_5-C_{12} cycloalkylene, or cycloalkylidene; and,

(b) a sulfur-containing diphenol represented by the structural formula:



wherein R and R^1 can each independently be H or C_1-C_4 alkyl, and n is 1 or 2, said sulfur-containing diphenol being present in an amount sufficient to provide a sulfur content in said composition in the range about 3-13 percent by weight based upon the weight of said composition.

16. The composition of claim 15 wherein said non-polycyclic, sulfur-free diphenol and said sulfur-containing diphenol are polymers present in the form of a physical mixture.

17. The composition of claim 16 wherein one or more of said non-polycyclic, sulfur-free diphenol polymers and one or more of said sulfur-containing diphenol polymers are chemically bonded to each other in the form of block copolymers, random copolymers, alternating copolymers, and mixtures thereof.

18. The composition of claim 15 wherein said non-polycyclic, sulfur-free diphenol and said sulfur-containing diphenol are polymers chemically bonded to each other.

19. The composition of claim 18 wherein one or more of said non-polycyclic, sulfur-free diphenol polymers and one or more of said sulfur-containing diphenol polymers are chemically bonded to each other in the form of block copolymers, random copolymers, alternating copolymers, and mixtures thereof.

20. The composition of claim 15 wherein said non-polycyclic, sulfur-free diphenol and said sulfur-containing diphenol are polymers present in the form of a blend comprising a physical mixture and moieties chemically bonded to each other.

21. The composition of claim 20 wherein one or more of said non-polycyclic, sulfur-free diphenol polymers and one or more of said sulfur-containing diphenol polymers are chemically bonded to each other in the form of block copolymers, random copolymers, alternating copolymers, and mixtures thereof.

22. The composition of claim 16 wherein said non-polycyclic, sulfur-free diphenol is selected from the group consisting of BPA, 4,4'-cyclohexylidenediphenol, 4,4'-cyclohexylidenebis(2-methylphenol); and mixtures thereof; and, said sulfur-containing diphenol is 4,4'-thiodiphenol.

23. The composition of claim 18 wherein said non-polycyclic, sulfur-free diphenol is selected from the group consisting of BPA, 4,4-cyclohexylidenediphenol, 4,4'-cyclohexylidenebis(2-methylphenol), and mixtures thereof; and, said sulfur-containing diphenol is 4,4'-thiodiphenol.

INTERNATIONAL SEARCH REPORT

International Application PCT/US81/01065

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.^{3} C08G 63/62; C08L 69/00

U.S. CL. 528/204, 528/171; 528/196; 525/469 ; 525/462

II. FIELDS SEARCHED

Minimum Documentation Searched[4]

Classification System	Classification Symbols
US	528/204; 528/171; 528/196 ; 525/462; 525/469

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched[5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[14]

Category *	Citation of Document,[16] with indication, where appropriate, of the relevant passages[17]	Relevant to Claim No.[18]
X	US, A, 2,999,846 PUBLISHED 12 SEPTEMBER 1961 SCHNELL ET AL	1-2, 9-15
X	US, A, 3,271,367 PUBLISHED 06 SEPTEMBER 1966 SCHNELL ET AL	1-2, 9-15
X	US, A, 3,359,238 PUBLISHED 19 DECEMBER 1967 GOLDBERG ET AL	1-2, 9-15
X	US, A, 3,398,212 PUBLISHED 20 AUGUST 1968 JACKSON ET AL	1-2, 9-15
X	US, A, 3,451,966 PUBLISHED 24 JUNE 1969 GREGORY ET AL	1-2, 9-15
X	US, A, 3,635,895 PUBLISHED 18 JANUARY 1972 KRAMER	1-2, 9-15
X	US, A, 3,737,409 PUBLISHED 5 JUNE 1973 FOX	1-2, 9-15
X	US, A, 3,912,688 PUBLISHED 14 OCTOBER 1975 SCHILLER ET AL	1-2, 9-15

* Special categories of cited documents:[15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search[2] 22 JANUARY 1982	Date of Mailing of this International Search Report[2] 03 FEB 1982
International Searching Authority[1] ISA/US	Signature of Authorized Officer[10] Harold D. Anderson HAROLD D. ANDERSON

International Application No. PCT/US81/01065

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	US, A, 4,043,980 PUBLISHED 23 AUGUST 1977 BARON ET AL	1-2, 9-15
X	US, A, 4,174,359 PUBLISHED 13 NOVEMBER 1979 SIVARAMAKRISHNAN ET AL	1-2, 9-15
X	DE, A, 2,727,595 PUBLISHED 01 DECEMBER 1977 BARON ET AL	1-2, 9-15
X	DE, B, 1,187,797 PUBLISHED 25 FEBRUARY 1965 SCHNELL ET AL	1-2, 9-15
X	US, A, 4,152,367, PUBLISHED 01 MAY 1979, BINSACK ET AL	3-8, 16-23

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers______, because they relate to subject matter [11] not required to be searched by this Authority, namely:

2.☐ Claim numbers______, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [12], specifically:

VI.☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

I. COPOLYCARBONATES: CLAIMS 1-2, 9-15
II. POLYCARBONATE BLENDS: CLAIMS 3-8, 16-23

1.☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (supplemental sheet (2)) (October 1977)