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(21) International Application Number: PCT/US86/00301 (22) International Filing Date: 13 February 1986 (13.02.86) (31) Priority Application Number: 701,838 (32) Priority Date: 14 February 1985 (14.02.85) (33) Priority Country: US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbot Road, Midland, MI 48640 (US). (72) Inventors: OGOE, Samuel, A. ; 308 Linden Street, Angleton, TX 77515 (US). FARAH, Hani ; 244 Lakewood Drive, Clute, TX 77531 (US). DICK, Kevin, F. ; 525 Sycamore Street, Lake Jackson, TX 77566 (US).		(74) Agent: RUSSELL, David, H.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: CARBONATE POLYMER COMPOSITIONS CONTAINING A SALT OF AN AROMATIC SULFONAMIDE AND A FREE AROMATIC SULFIMIDE (57) Abstract A carbonate polymer such as a bisphenol A homopolycarbonate containing a small amount of a metal salt of an aromatic sulfonamide and a free aromatic sulfimide resists combustion upon exposure to an ignition source, exhibits good optical properties and exhibits molecular weight stability. Optionally, a halogenated organic compound can be added to the composition. The carbonate polymer compositions of this invention are useful as air filters, fan housings, exterior automobile components, housings for electrical motors, appliances, business and office equipment, photographic equipment and lighting and aircraft applications.		

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CARBONATE POLYMER COMPOSITIONS CONTAINING A
SALT OF AN AROMATIC SULFONAMIDE AND A
FREE AROMATIC SULFIMIDE

This invention relates to carbonate polymer compositions containing additives which act as flame retardants and improve processing stability.

Carbonate polymers derived from reactions of
5 dihydroxyorganic compounds, particularly the dihydric phenols, and carbonic acid derivatives such as phosgene, have found extensive commercial application because of their excellent physical properties. These thermoplastic polymers are suitable for the manufacture of molded
10 parts wherein impact strength, rigidity, toughness, heat resistance and excellent electrical properties are required.

Unfortunately, however, these polymers exhibit a brief but definite burning time when contacted with
15 an open flame. More importantly, as is often the case, the carbonate polymers contain stabilizers and other

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additives which are often more combustible than the unmodified carbonate polymer. As a result, the modified carbonate polymers frequently exhibit substantially poorer resistance to combustion than does the unmodified carbonate polymer.

In attempts to increase the combustion resistance of carbonate polymers including the modified forms thereof, it has been a common practice to employ monomeric phosphites, phosphoric acid esters, thiophosphoric acid esters containing halogenated alkyl radicals and halogenated organic compounds into the carbonate polymer. However, in order to obtain any noticeable improvement in combustion resistance, these additives have been employed in such large quantities that they often adversely affect many of the desirable physical and mechanical properties of the carbonate polymer.

More recently, for example as taught in U.S. Patent No. 4,254,015; metal salts of aromatic sulfonamides are employed as fire retardant additives in order to retard the combustion of carbonate polymers which are exposed to a low temperature ignition source. Unfortunately, the use of such salts as ignition resistant additives to carbonate polymers can adversely affect the processing stability of the carbonate polymer. As a result, carbonate polymers containing such ignition resistant salt additives can exhibit undesirable molecular weight degradation and can adversely affect optical properties.

In view of the deficiencies of the conventional fire retardant carbonate polymer compositions, it would be highly desirable to provide a carbonate polymer

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composition having improved resistance to burning when exposed to an ignition source, and which composition exhibits good molecular weight stability and optical stability upon processing.

5 The present invention is a carbonate polymer composition comprising a carbonate polymer having dispersed therein (1) a salt of an aromatic sulfonamide, said salt being represented by the formula



wherein Ar is an aromatic group, R is a monovalent organic moiety, M is a cation, and n is a number corresponding to the valence of M, in an amount sufficient to retard combustion when the composition is exposed to an ignition source, and (2) a functionally effective amount of a free aromatic sulfimide, said free aromatic sulfimide and amount thereof being selected to provide a desirable degree of molecular weight stability to the carbonate polymer composition upon thermal processing thereof.

Optionally, the carbonate polymer composition of the present invention further comprises a functionally effective amount of a halogenated organic compound.

25 The fire retardant carbonate polymer compositions of the present invention provide the skilled artisan with a process for providing carbonate polymer compositions which are useful when exposed to an ignition source. Of particular interest are those applications wherein the ignition source is a low temperature

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ignition source. Said compositions are suitably employed in most applications in which polycarbonates have been previously utilized. Applications of particular interest for the utilization of the said carbonate polymer compositions of this invention are as follows: air filters, fan housings, exterior automobile components, housings for electrical motors, appliances, business and office equipment, photographic equipment, and lighting and aircraft applications.

10 The carbonate polymers employed in the present invention are advantageously aromatic carbonate polymers such as the trityl diol carbonates described in U.S. Patent Nos. 3,036,036; 3,036,037; 3,036,038 and 3,036,039; polycarbonates of bis(ar-hydroxyphenyl)-
15 alkylidenes (often called bisphenol-A type diols) including their aromatically and aliphatically substituted derivatives such as disclosed in U.S. Patent Nos. 2,999,835; 3,038,365 and 3,334,154; and carbonate polymers derived from other aromatic diols such as
20 described in U.S. Patent No. 3,169,121.

 It is understood, of course, that the polycarbonate may be derived from (1) two or more different dihydric phenols or (2) a dihydric phenol and a glycol or a hydroxy- or acid-terminated polyester or a dibasic
25 acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired. Also suitable for the practice of this invention are blends of any one of the above carbonate polymers. Also included in the term "carbonate polymer" are the ester/carbonate
30 copolymers of the types described in U.S. Patent Nos. 3,169,121; 4,287,787; 4,156,069; 4,260,731; 4,330,662; 4,360,656; 4,374,973; 4,225,556; 4,388,455; 4,355,150

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and 4,105,633. Of the aforementioned carbonate polymers, the polycarbonates of bisphenol-A and derivatives, including copolycarbonates of bisphenol-A, are preferred. Methods for preparing carbonate polymers for use in the practice of this invention are well known, for example, several suitable methods are disclosed in the aforementioned patents.

The salt form of aromatic sulfonamides which are employed herein are represented by the formula:



wherein Ar is an aromatic group, R is a monovalent organic moiety, M is a suitable cation such as a metal cation and n is a number corresponding to the valence of M. M is preferably an alkali metal. Alternatively, M is a divalent cation preferably alkali earth or multivalent cation such as, for example, those obtained from copper, aluminum, and antimony. Representative preferred sulfonamide salts include the alkali metal salts of saccharin, N-(p-tolylsulfonyl)-p-toluenesulfonamide, N-(N'-benzylaminocarbonyl)sulfanilamide, N-(phenylcarboxyl)-sulfanilamide, N-(2-pyrimidinyl)sulfanilamide, N-(2-thiazolyl)sulfanilamide and other salts of the sulfonamides disclosed in U.S. Patent No. 4,254,015. Combinations of the above-identified salts can also be employed.

The halogenated organic compound can be virtually any halogenated organic compound commonly used as a fire retardant additive. A functionally

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effective amount of halogenated organic compound is that amount which provides fire retardant character to the carbonate polymer. The preferred compounds are the halo-substituted aromatic compounds (halo is fluoro, 5 chloro, or bromo). Suitable compounds include, for example, decabromo diphenyloxide, tris(tribromophenoxy)-triazine, decabromo diphenyl carbonate, a tetrafluoro-ethylene polymer, an oligomer or polymer of tetrabromobisphenol A, and a copolymer of bisphenol A/tetrabromobisphenol A. 10 Combinations of the above-identified compounds can be employed. Examples of other suitable monomeric and polymeric halogenated compounds are disclosed in U.S. Patent No. 4,263,201.

The free aromatic sulfimide of this invention 15 is suitably any free imide compound in acid form. Typically, such a compound is one which is capable of introducing a buffering character to the carbonate polymer composition containing an amount of the aforementioned salt form of the aromatic sulfonamide. 20 Typically, the pKa of the imide compound ranges from 1 to 3. Preferred free aromatic sulfimides are the sulfimides described as free sulfonamides disclosed in U.S. Patent No. 4,254,015. Such free aromatic sulfimides are advantageously represented by the formula:



where Ar is an aromatic group. It is believed that a functionally effective amount of the free aromatic sulfimide component provides the desired molecular weight stability and maintains the desirable optical 30 properties to the carbonate polymer composition containing the salt form of the aromatic sulfimide.

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The fire retardant carbonate polymer compositions of the present invention are suitably prepared by combining the carbonate polymer with an effective amount of fire retardant additive using any of a variety of blending procedures conventionally employed for incorporating additives into carbonate polymer resins. For example, dry particulates of the carbonate polymer and the fire retardant additive can be dry blended and the resulting dry blend extruded and molded into the desired shape. By "effective amount" is meant that combination of the desired fire retardant additive components is sufficient to provide fire retardant character to the carbonate polymer with which it is blended.

While any amount of fire retardant additive that imparts to the carbonate polymer an improved fire retardancy is suitable, that amount of additive which provides an effective amount of fire retardancy to the carbonate polymer in combination with the maintenance of good processing stability and desirably good optical properties is particularly desirable. Preferred amounts of components typically range from 0.001 to 2, more preferably 0.01 to 0.5 weight percent salt of an aromatic sulfonamide; from 0 to 20, more preferably from 0.01 to 10, most preferably from 0.01 to 5 weight percent halogenated organic compound; and from 0.001 to 2, more preferably 0.01 to 0.5 weight percent free aromatic sulfimide. All weights are based on the weight of carbonate polymer to which the components are added.

In addition to the aforementioned fire retardant additives, other additives can be included in the carbonate polymer composition of the present invention

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such as fillers (i.e., a tetrafluoroethylene polymer or glass fibers), pigments, dyes, antioxidants, stabilizers, ultraviolet light absorbers, mold release agents and other additives commonly employed in carbonate
5 polymer compositions.

The following examples are given to further illustrate the invention and should not be construed as limiting its scope. In the following examples, all parts and percentages are by weight unless otherwise
10 indicated.

Examples 1, 2, 3 and Comparative Runs A and B

Example 1 is prepared using a bisphenol-A polycarbonate pellet heat stabilized with an organo phosphorus compound as described in U.S. Patent
15 No. 4,474,937, along with 0.06 percent para-tolylsulfimide (HPTSM), 0.6 percent phenoxy terminated tetrabromo bisphenol-A carbonate oligomer having an average of 5 repeating units (TBBPAC), and 0.06 percent potassium para-tolylsulfimide (KPTSM). The components are
20 mixed for about 5 minutes and the mixture is extruded into pellets at 550°F (288°C) on a twin screw extruder. The pellets are dried on a force draft oven at 250°F (121°C). A portion of the resulting example is subjected to melt shearing at 540°F (282°C) by a torque
25 rheometer for over 30 minutes. The initial and final molecular weight of the example so treated is presented in Table I. The remainder of the example is injection molded at 575°F (302°C) into bars and disks for flammability and optical properties.

30 In a similar manner, Example 2 is prepared using the heat stabilized polycarbonate, 0.06 percent KPTSM, 0.09 percent HPTSM and 0.6 percent TBBPAC.

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In a similar manner, Example 3 is prepared using the heat stabilized polycarbonate, 0.06 percent KPTSM, 0.12 percent HPTSM and 0.6 percent TBBPAC.

Comparative Run A is the heat stabilized
5 polycarbonate.

In a similar manner to Example 1, Comparative Run B is prepared using the heat stabilized polycarbonate, 0.06 percent KPTSM and 0.6 percent TBBPAC.

Evaluations of the Examples and Comparative
10 Runs are presented in Table I.

TABLE I

Examples and Comp. Runs	Polycarbonate Molecular Weight		U-94 Test (1)		Optical Properties (2)		
	Initial	Final	Ave. T. (sec)	No. Drips	Rating	Trans.	
						YI (Percent)	Haze (Percent)
1	27,200	25,300	1,900	1.7	0/5	V-0	2.7 90.2 1.7
2	27,200	25,400	1,800	1.5	0/5	V-0	2.6 90.2 1.8
3	27,100	25,600	1,500	1.4	0/5	V-0	1.5 90.3 1.9
A	27,250	25,800	1,470	10	5/5	V-2	2.5 90.3 1.4
B	27,000	21,000	6,000	2.6	0/5	V-0	2.8 89.9 1.4

(1) Tests are performed on a 1/8 inch (3.175 mm) molded bar. Ave. T. is the average flame time in seconds for 5 bars. No. Drips is the number of bars that drip per 5 bars tested.

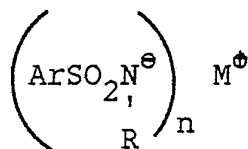
(2) YI is yellowness index; Trans (percent) is percent transmittance; Haze (percent) is percent haze.

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The data in Table I indicate that Examples 1, 2 and 3 exhibit good ignition resistant properties and improved processing stability as indicated by the low change in molecular weight. Correspondingly, Comparative Run B exhibits a large change in molecular weight upon evaluations. Examples 1, 2 and 3 exhibit compatibility of the HPTSM with the carbonate polymer as is illustrated by the negligible change in optical properties of the samples over an untreated sample such as Comparative Run A.

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1. A carbonate polymer composition comprising a carbonate polymer having dispersed therein (1) a salt of an aromatic sulfonamide, said salt being represented by the formula



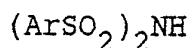
wherein Ar is an aromatic group, R is a monovalent organic moiety, M⁺ is a cation, and n is a number corresponding to the valence of M, in an amount sufficient to retard combustion when the composition is exposed to an ignition source, and (2) a functionally effective amount of a free aromatic sulfimide, said free aromatic sulfimide and amount thereof being selected to provide a desirable degree of molecular weight stability to the carbonate polymer composition upon thermal processing thereof.

2. The composition of Claim 1 wherein said carbonate polymer is a homopolycarbonate of bisphenol A.

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3. The composition of Claim 1 wherein said free aromatic sulfimide exhibits a pKa of from 1 to 3.

4. The composition of Claim 3 wherein said free aromatic sulfimide is represented by the formula:



wherein Ar is an aromatic group.

5. The composition of Claim 1 wherein the amount of said salt of an aromatic sulfonamide ranges from 0.001 to 2 weight percent and the amount of said free aromatic sulfimide ranges from 0.001 to 2 weight percent, based on the weight of the carbonate polymer.

6. The composition of Claim 5 wherein the amount of said salt of an aromatic sulfonamide ranges from 0.01 to 0.5 weight percent and the amount of said free aromatic sulfimide ranges from 0.01 to 0.5 weight percent, based on the weight of the carbonate polymer.

7. The composition of Claim 1 wherein said salt of an aromatic sulfonamide is potassium p-tolylsulfimide and said free aromatic sulfimide is p-tolylsulfimide.

8. The composition of Claim 1 which further comprises a functionally effective amount of a halogenated organic compound.

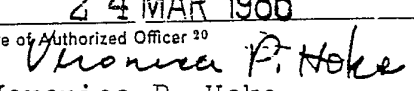
9. The composition of Claim 9 wherein said halogenated organic compound is a halogenated aromatic compound.

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10. The composition of Claim 8 wherein the amount of said halogenated organic compound is up to 20 weight percent, based on the weight of the carbonate polymer.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/00301

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.4 C08K 5/43 U.S. CL. 524/83, 159, 167, 168						
II. FIELDS SEARCHED Minimum Documentation Searched ⁴ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="text-align: center; padding: 10px 0;">U.S.</td> <td style="text-align: center; padding: 10px 0;">524/83, 159, 167, 168</td> </tr> </table> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵			Classification System	Classification Symbols	U.S.	524/83, 159, 167, 168
Classification System	Classification Symbols					
U.S.	524/83, 159, 167, 168					
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				
Y	US, A, 4,254,015 THOMAS ET AL PUBLISHED 03 MARCH 1981	1-10				
Y	US, A, 4,486,560 THOMAS PUBLISHED 04 DECEMBER 1984	1-10				
* Special categories of cited documents: ¹⁵ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published 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; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search ² 13 MARCH 1986		Date of Mailing of this International Search Report ² 24 MAR 1986				
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