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(54) Title: FLAME RETARDANT POLYPHENYLENE ETHER COMPOSITION CONTAINING BROMINATED POLYSTYRENE AND ANTIMONY OXIDE

(57) Abstract

The flame resistance of blends of polyphenylene ether resin and high impact polystyrene is upgraded by including both a brominated polystyrene and antimony oxide, which work in synergistic combination in the compositions. The present flame retardant combination not only exhibits good heat stability, but unlike many prior art flame retardants of greater volatility, also resists migration to the surface.

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FLAME RETARDANT POLYPHENYLENE ETHER COMPOSITION CONTAINING BROMINATED POLYSTYRENE AND ANTIMONY OXIDE

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to flame retardant polyphenylene ether compositions and, more specifically, to blends of a polyphenylene ether resin and a high impact polystyrene in which a post-brominated polystyrene oligomer or polymer and antimony oxide are used in combination to impart better flame resistance.

2. DESCRIPTION OF THE PRIOR ART

Thermoplastic compositions of polyphenylene ether (oxide) resins and high impact polystyrenes are known to be useful for injection molding into a variety of articles characterized by highly desirable property profiles. With the wider use of these compositions in products where good flame resistance is an important requirement, the need has grown for additives that upgrade the flame retardance of the composition without significantly detracting from other desired properties. Most flame retardant additives for polyphenylene ether compositions have been non-polymeric compounds that are relatively low in molecular weight. Many of these tend to juice or bloom, that is, in essence to volatilize or migrate to the surface of the composition during the molding process.

Recent efforts have involved the investigation of higher molecular weight materials, and especially styrene oligomers and polymers having bromine substituents bound in the chain. For instance, U.S. Patent 4,279,808 (Hornbaker, et al.) describes moldable thermoplastic resins formed by the polymerization of nuclear brominated styrenes in the presence of rubber. The resulting resin is useful as such but can also be blended with other resins, including polyphenylene oxides, to impart increased flame resistance to the blend.

A number of other patents describe compositions of polyphenylene ether and polystyrene in which the polystyrene can theoretically contain flame retardant halogen atoms such as bromine or chlorine. These include U.S. Patent 3,933,941 (Yonemitsu, et al.), U.S. Patent 4,355,126 (Haaf, et al.) and U.S. Patent 4,448,931 (Sugio, et al.).

Also of interest are recent developments in which various copolymers of styrene and bromostyrene are included in polyphenylene ether resin blends to improve the flame resistance. These are the subject of pending U.S. continuation applications Serial No. 762,805 and Serial No. 762,806, of August 2, 1985(both in the names of Glenn D. Cooper and Arthur Katchman), as well as pending U.S. applications Serial No. 675,344 of November 27, 1984 (Abolins, Aycock and Kinson) and Serial No. 675,715 of November 28, 1984(Axelrod and Cooper). Laid open United Kingdom applications 2076830A and 2076831A are essentially foreign counterparts of the first two above mentioned U.S. applications.

Several patents describe the preparation of brominated polystyrene oligomers having fire retardant utility. Such materials are prepared by the action of elemental bromine on the hydrogenated polystyrene oligomer as disclosed in U.S. Patents 4,074,033 and 4,143,221 (Naarmann, et al.). The usefulness of brominated styrene oligomers for certain polymers is described in Wurmb, et al., U.S. Patent 4,107,231 (for linear polyesters), in Theysohn, et al., U.S. Patent 4,137,212 (for nylon compositions), and in Neuberg, et al., U.S. Patent 4,151,223 (for fibrous or filamentous linear thermoplastic polyesters).

Japan patent 90,256(1985) describes a flame retardant polyphenylene ether composition said to exhibit excellent flame retardance and heat resistance, with very little migration of halogenated materials. The composition comprises, in addition to the polyphenylene ether resin, a brominated styrene polymer and optionally other styrene polymers such as rubber modified polystyrene and SBR triblock copolymers. A particular brominated styrene polymer shown is PYRO-CHEK 68PB, which is described as a brominated polystyrene containing 68 per cent bromine and having a number average molecular weight of 150,000.

SUMMARY OF THE INVENTION

With the present invention, the discovery has been made that useful, flame retardant blend compositions of a polyphenylene ether resin and a high impact polystyrene can be made by incorporating a brominated styrene oligomer or polymer in conjunction with antimony oxide. The resulting compositions provide, in addition to good flame retardant properties, excellent resistance to migration and blooming, as well as good thermal stability and toxicological safety.

The blends are extrudable and moldable into a broad spectrum of shaped plastic products.

DESCRIPTION OF THE INVENTION

Briefly described, the compositions of the present invention comprise thermoplastic blends of

(a) a polyphenyene ether resin;

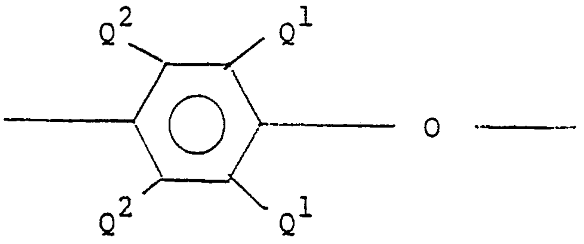
(b) a rubber modified, high impact polystyrene resin;

(c) a brominated polystyrene in an amount which improves the flame retardancy of the combination of (a) and (b); and

(d) antimony oxide in an amount which synergistically enhances the flame retardancy of the combination of (a), (b) and (c).

The polyphenylene ethers(also known as polyphenylene oxides) used in the present invention are a well known class of polymers which have become very useful commercially as a result of the discovery by Allan S. Hay of an efficient and economical method of production (See, for example, U.S. Patents 3,306,874 and 3,306,875, which are incorporated herein by reference). Numerous modifications and variations have since been developed but, in general, they are characterized as a class by the presence of arylenoxy structural units. The present invention includes all such variations and modifications, including but not limited to those described hereinafter.

The polyphenylene ethers favored for use in the practice of this invention generally contain structural units of the following formula



(I)

in which in each of these units independently each Q^1 is hydrogen, halogen, primary or secondary lower alkyl (i.e., alkyl containing up to 7 carbon atoms), phenyl, haloalkyl or aminoalkyl wherein at least two carbon atoms separate the halogen or nitrogen atom from the benzene ring, hydrocarbonoxy, or halohydrocarbonoxy wherein at least two carbon atoms separate the halogen and oxygen atoms; and each Q^2 is independently hydrogen, halogen, primary or secondary lower alkyl, phenyl, haloalkyl, hydrocarbonoxy or halohydrocarbonoxy as defined for Q^1. Examples of suitable primary lower alkyl groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, isoamyl, 2-methylbutyl, n-hexyl, 2,3-dimethylbutyl, 2-,3- or 4-methylpentyl and the corresponding heptyl groups. Examples of secondary lower alkyl groups are isopropyl, sec-butyl and 3-pentyl. Preferably, any alkyl radicals are straight chain rather than branched. Most often, each Q^1 is alkyl or phenyl, especially C_{1-4} alkyl, and each Q^2 is hydrogen.

Both homopolymers and copolymers are included. Suitable homopolymers are those containing, for example, 2,6-dimethyl-1,4-phenylene ether units. Suitable copolymers include random copolymers containing such units in combination with, for example, 2,3,6-trimethyl-1,4-phenylene ether units. Many suitable random copolymers, as well as homopolymers, are disclosed in the patent literature, including various Hay patents. Also contemplated are graft copolymers, including those prepared by grafting onto the polyphenylene ether chain such vinyl monomers as acrylonitrile and vinyl aromatic compounds (for example, styrene), and such polymers as polystyrenes and elastomers. Still other suitable polyphenylene ethers are the coupled polyphenylene ethers in which the coupling agent is reacted with the hydroxy groups of the two polyphenylene ether chains to increase the molecular weight of the polymer. Illustrative of the coupling agents are low molecular weight polycarbonates, quinones, heterocycles and formals.

The polyphenylene ether generally has a molecular weight (number average, as determined by gel permeation chromatography, whenever used herein) within the range of about 5,000 to 40,000. The intrinsic viscosity of the polymer is usually in the range of about 0.40 to 0.5 deciliters per gram (dl./g.), as measured in solution in chloroform at 25°C.

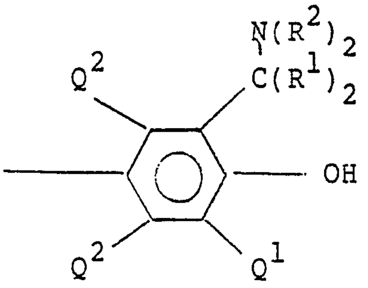
The polyphenylene ethers may be prepared by known methods, and typically by the oxidative coupling of at least one corresponding monohydroxyaromatic (e.g., phenolic) compound. A particularly useful and readily available monohydroxyaromatic compound is 2,6-xylenol (in which for the above formula each Q^1 is methyl and each Q^2 is hydrogen), the corresponding polymer of which may be characterized as a poly(2,6-dimethyl-1,4-phenylene ether).

Any of the various catalyst systems known in the art to be useful for the preparation of polyphenylene ethers can be used in preparing those employed in this invention. For the most part, they contain at least one heavy metal compound, such as a copper, manganese or cobalt compound, usually in combination with various other materials.

Among the preferred catalyst systems are those containing copper. Such catalysts are disclosed, for example, in the aforementioned U.S. Patents 3,306,874 and 3,306,875, and elsewhere. They are usually combinations of cuprous or cupric ions, halide ions (i.e., chloride, bromide or iodide), and at least one amine.

Also preferred are catalyst systems containing manganese. They are generally alkaline systems containing divalent manganese and such anions as halide, alkoxide or phenoxide. Most often, the manganese is present as a complex with one or more complexing and/or chelating agents such as dialkylamines, alkanolamines, alkylenediamines, o-hydroxyaromatic aldehydes, o-hydroxyazo compounds, ω-hydroxyoximes (both monomeric and polymeric), o-hydroxyaryl oximes, and α-diketones. Also useful are cobalt-containing catalyst systems. Those skilled in the art will be familiar with patents disclosing manganese and cobalt-containing catalyst systems for polyphenylene ether preparation.

Especially useful polyphenylene ethers for the purposes of this invention are those which comprise molecules having at least one of the end groups of formulas II and III, below, in which Q^1 and Q^2 are as previously defined, each R^1 is independently hydrogen or alkyl, providing that the total number of carbon atoms in both R^1 radicals is 6 or less, and each R^2 is independently hydrogen or a C_{1-6} primary alkyl radical. Preferably, each R^1 is hydrogen and each R^2 is alkyl, especially methyl or n-butyl.



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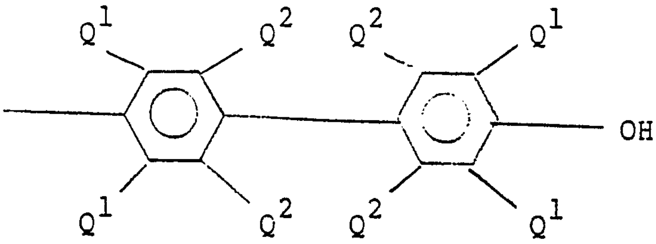
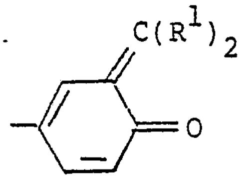


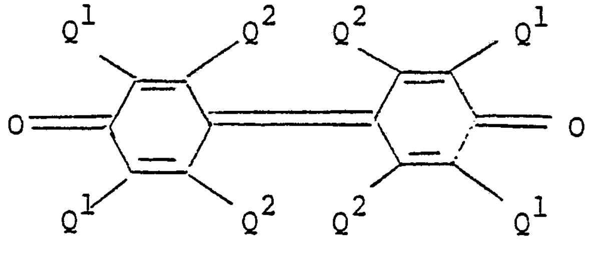
(III)

Polymers containing the aminoalkyl-substituted end groups of formula II may be obtained by incorporating an appropriate primary or secondary monoamine as one of the constituents of the oxidative coupling reaction mixture, especially when a copper- or manganese-containing catalyst is used. Such amines, especially the dialkylamines and preferably di-n-butylamine and dimethylamine, frequently become chemically bound to the polyphenylene ether, most often by replacing one of the α-hydrogen atoms on one or more Q^1 radicals adjacent to the hydroxy group on the terminal unit of the polymer chain. During further processing and/or blending, the aminoalkyl-substituted end groups may undergo various reactions, probably involving a quinone methide-type intermediate of formula IV, below (R^1 is defined as above), with beneficial effects often including an increase in impact strength and compatibilization with other blend components.



(IV)

Polymers with biphenol end groups of formula III are typically obtained from reaction mixtures in which a by-product diphenoquinone of formula V, below, is present, especially in a copper-halide-secondary or tertiary amine system. In this regard, the disclosures of the U.S. Patents 4,234,706, 4,477,649 and 4,482,697 are particularly pertinent, and are incorporated herein by reference. In mixtures of this type, the diphenoquinone is ultimately incorporated into the polymer in substantial amounts, chiefly as an end group.



(V)

In many polyphenylene ethers obtained under the conditions described above, a substantial proportion of the polymer molecules, usually as much as about 90% by weight of the polymer, contain end groups having one or frequently both of formulas II and III. It should be understood, however, that other end groups may be present and that the invention in its broadest sense may not be dependent on the molecular structures of the polyphenylene ether end groups.

It will thus be apparent to those skilled in the art that a wide range of polymeric materials encompassing the full recognized class of polyphenylene ether resins are contemplated as suitable for use in the practice of the present invention.

The rubber modified, high impact polystyrene useful as component (b) in the present compositions can be selected from any of the materials known generally in the art as high impact polystyrenes, or HIPS. In general, these modified polystyrene resins are made by adding rubber during or after polymerization of the styrene, to yield an interpolymer of rubber and polystyrene, a physical admixture of rubber and polystyrene, or both, depending on the particular process employed.

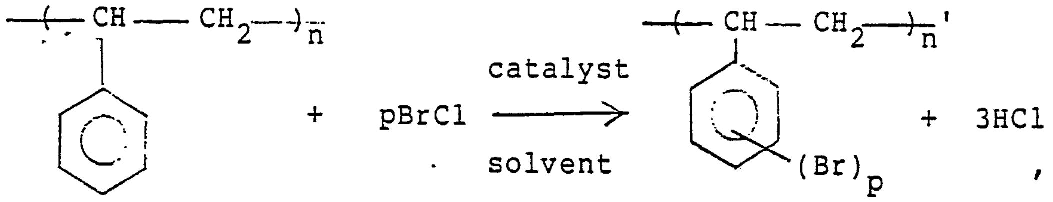
Suitable rubber modifiers include polybutadiene, polyisoprene, polychloroprene, ethylene-propylene copolymers (EPR), ethylene-propylene-diene (EPDM) rubbers, styrene-butadiene copolymers (SBR), and polyacrylates. The amount of rubber employed will vary, depending on such factors as the process of manufacture and individual requirements.

Included within this family of materials for purposes of the present invention are more recently developed forms in which such factors as the rubber particle size, the gel and cis contents of the rubber phase, and the rubber volume percent are regulated or controlled to achieve improvements in the impact resistance and other properties. These kinds of HIPS are described in the patent literature, including U.S. Patent 4,128,602 (Abolins, Katchman and Lee, Jr.), and U.S. Patent 4,528,327 (Cooper and Katchman), which are incorporated herein by reference.

Also contemplated as suitable for use are high impact polystyrenes having morphological forms which are sometimes referred to as core-shell, comprising particles of rubber encapsulated polystyrene dispersed in a matrix of polystyrene resin. Examples of this type are disclosed in U.S. Patent 4,513,120 (Bennett, Jr. and Lee, Jr.), incorporated herein by reference, as well as the above-mentioned U.S. 4,528,327.

The brominated polystyrene can be prepared by following the procedures described in published European patent application 0047549 of Henry J. Barda. In general, the method of preparation comprises dissolving a polystyrene having a molecular weight of at least 20,000 in a solvent, and reacting the dissolved polystyrene with a stoichiometric excess of bromine chloride (that is, an amount greater than that required for achieving the desired, theoretical degree of bromination), in the presence of up to about 15% by weight of a Lewis acid catalyst, based on the weight of the polystyrene, at temperatures of about 20°C. to about 50°C.

The bromination reaction can be represented by the following equation:



where n and n' represent the number of styrene monomer units in the respective polystyrene chains; and p represents the number, as an average, of bromine atoms added to (and displacing a corresponding number of hydrogen atoms from) the aromatic nucleus of each styrene monomer unit and is preferably from 1 to 3. As shown, hydrogen chloride is produced as a byproduct of the reaction.

The polystyrene reactant employed may be either an oligomer or polymer. If the initial molecular weight of the polystyrene is in the range from about 20,000 to about 50,000, brominated polystyrene oligomers can be produced of recognized value as fire retardant additives. It is preferred to carry out the bromination reaction using a polystyrene reactant having a molecular weight of about 100,000 or more, and especially 150,000 or higher.

The molecular weight of the polystyrene reactant is determined by gel permeation chromatography, as a weight average molecular weight. It can also be determined by light scattering, as an alternative approach.

The polystyrene reactant may be a halo- or lower alkyl-substituted polymer, or a copolymer such as of styrene and alpha-methyl styrene. It is in any event not rubber modified, and is thus distinguishable on that basis alone from component (b) in the compositions.

The catalyst is preferably a metal halide Lewis acid catalyst that is capable of effecting a Friedel-Crafts reaction. These include the bromides and chlorides of aluminum, antimony, and mixtures thereof. Specific examples are $SbCl_3$, $SbCl_5$, $SbBr_3$, $SbClBr_4$, $SbBrCl_4$, $FeCl_3$, $FeBr_3$, $AlCl_3$, $TiCl_4$, $TiBr_4$, $SnCl_2$, $SnCl_4$, $AlBr_3$, $BeCl_2$, $CdCl_2$, $ZnCl_2$, BF_3, BCl_3, BBr_3, $BiCl_3$ and $ZrCl_4$, as well as mixtures thereof. Especially preferred is antimony trichloride($SbCl_3$).

The amount of catalyst employed should be at least 2% by weight, based on the weight of the polystyrene reactant. Catalyst levels in the range from about 5% to about 8% are preferred.

In general, the reaction is feasible using small amounts of catalyst and large amounts of bromine chloride in excess of the theoretical amount or, conversely, large amounts of catalyst and small amounts of bromine chloride over the theoretical amount.

The organic solvent selected as the reaction medium should ideally dissolve the reactants, be substantially anhydrous, and be inert or exhibit relatively low reactivity toward the reactants. Organic solvents free of carbon-to-carbon unsaturation have been found to be suitable. Especially useful are halogenated, particularly chlorinated, saturated aliphatic hydrocarbons. Examples include carbon tetrachloride, chloroform, tetrachloroethane, methylene chloride, trichloroethane, dibromoethane, and the like. The most preferred is ethylene dichloride.

Any unreacted bromine chloride may be removed by distillation, or by chemical elimination as by adding an aqueous solution of bisulfite or caustic.

The brominated polystyrene product can be recovered by adding the still warm reaction mixture to hot methanol, upon which the product precipitates in finely particulate form, with good color. Alternatively, and less preferably, evaporation of the solvent will result in isolation of the brominated polystyrene.

Typically, using the aforementioned procedure a degree of bromine substitution of from one to three bromine atoms per aromatic nucleus on the average is achieved, depending on the particular conditions and especially the amount of bromine chloride used in relation to the amount of polystyrene reactant. An essentially tribrominated product is most desired. For the tribrominated products, the dominant substitution pattern is apparently at the 2, 4 and 5 positions on the aromatic nucleus, with lesser amounts of others isomers, including 2,3,5. A very small percentage of chlorine is believed to be nuclear bound also, but it is not considered significant for the purposes of this description.

In formulating the compositions in accordance with this invention, amounts for the above mentioned ingredients are selected which preferably fall within certain preferred ranges, as follows:

Ingredients	Amount, Parts by Weight
(a) Polyphenylene ether	10 to 90
(b) High impact polystyrene	90 to 10
TOTAL:	100 parts by weight
(c) Brominated polystyrene	6 to 18
(d) Antimony oxide	2 to 6

per 100 parts by (a) and (b).

The present kinds of compositions can also be formulated to include other ingredients in addition to those just described. These may be selected from among conventional materials commonly employed in polyphenylene ether resin blends, some of which are non-polymeric, others of which can be polymeric. Examples are plasticizers, mold release agents, melt viscosity reducers, colorants, stabilizers, antioxidants, mineral fillers (for example, clay), glass reinforcements, titanium oxides, lubricants, and so forth. Conventional amounts varying, for example, from less than 1 to greater than 50 percent by weight, per 100 percent by weight of the total composition, may be utilized.

The compositions can be prepared by any convenient method and, preferably, by forming a preblend of the ingredients, compounding the preblend by passing it through an extruder, and cooling the extrudate and cutting it into pellets or tablets. The tabletted composition can later be formed into the desired article, as by molding at elevated temperatures.

Because of their thermoplastic nature, the present compositions are particularly suitable for injection molding processes. Using standard procedures and conditions, these blends can be molded to various shapes and sizes, and the resulting products, besides having good flame retardancy, are characterized by excellent resistance to migration and blooming, good heat resistance, and good toxicological properties.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

The invention is further illustrated in the description below, which is set forth to show a preferred or best embodiment.

EXAMPLE

The composition shown in Table 1 was prepared by forming a dry blend of the ingredients, compounding the blend by passage through a 28mm Werner Pfleiderer twin-screw extruder at about 570°F. melt temperature, and cooling and chopping the extrudate into pellets. The pellets were molded into 0.125 inch-thick miniature test pieces, using a 4 ounce Newbury injection molding machine, a 500°F. melt temperature, and a 170°F. mold temperature. In addition, using the same conditions, molded test pieces having the dimensions 0.06 inch by 0.5 inch by 5 inches were prepared for the UL Subject 94 flame resistance test, and 4-inch (diameter) test discs were prepared for yellowness index and Gardner impact resistance measurements.

TABLE 1. Composition

Ingredients	Amount, Parts by Weight
Poly(2,6-dimethyl-1,4-phenylene ether)resin (PPO®, General Electric Co., i.v. 0.47 dl./g., chloroform, 25°C.)	25
Rubber modified, high impact polystyrene (FG 834, American Hoechst Co.)	75
Diphenyl decyl phosphite	0.5
Polyethylene	1.5
Zinc sulfide	0.15
Zinc oxide	0.15
Brominated polystyrene (PYRO-CHECK 68PB, Ferro Corp.)	13.2
Antimony oxide (KR, Harshaw Chemical Co.)	4.4

The brominated polystyrene employed (PYRO-CHEK 68PB, Ferro Corporation) had the following characteristics:

Bromine Content	68%
Softening Point(DSC)	220°C.
Specific Gravity	2.8
Volatiles (TGA-1 hr. @ 245°C)	0.25
(1) initial loss	230°C.
(2) 1% loss	340°C.
(3) 10% loss	408°C.
Color, Gardner instrument	
L =	93.5
a =	0.0
b =	9.0

The various test pieces were exposed to common physical properly tests in accordance with ASTM procedures and UL Subject 94 flame resistance procedures. The results are reported in Table 2.

TABLE 2. Properties

Tensile Strength	6900 psi
Elongation	67%
Notched Izod Impact Resistance	1.8 ft.lb./in. of notch
Gardner Impact Strength	5 in. lbs.
Deflection Temperature, under load at 264 psi	215°F.
Channel Flow Length, upon injection at 500°F. under 10,000 psi	16.5 inches
Melt Viscosity, at 500°F. and 1500^{-1} sec.	1910 poise
UL Subject 94 Test	
1/16-inch thick samples	VO (3.6)
1/8-inch thick samples	VO (3.0)
Yellowness Index	39.2

Other modifications and variations of this invention are possible and are contemplated as within the scope of this invention. It should be understood, therefore, that changes may be made in the particular embodiments shown without departing from the principles of the invention or sacrificing its chief benefits.

CLAIMS:

1. A flame retardant thermoplastic composition comprising

(a) a polyphenylene ether resin;

(b) a rubber modified, high impact polystyrene resin;

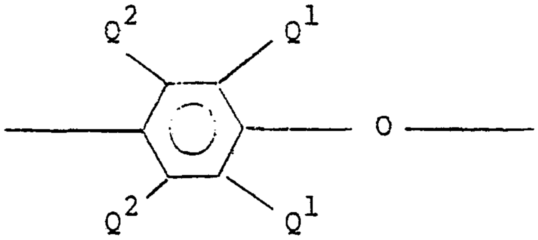
(c) a brominated polystyrene oligomer or polymer in an amount which improves the flame retardancy of the combination of (a) and (b); and

(d) antimony oxide in an amount which synergistically enhances the flame retardancy of the combination of (a), (b) and (c).

2. The compositions of Claim 1, in which component (a) is present in an amount from about 10 to about 90 parts by weight and component (b) is present in an amount from about 90 to about 10 parts by weight, based on 100 parts by weight of (a) and (b) combined.

3. The composition of Claim 2, in which component (c) is present in an amount from about 6 to about 18 parts by weight and component (d) in an amount from about 2 to about 6 parts by weight, for each 100 parts by weight of (a) and (b) combined.

4. The composition of Claim 1, in which the polyphenylene ether is a homopolymer or copolymer containing structural units of the formula



in which for each of these units independently each Q^1 is hydrogen, halogen, primary or secondary lower alkyl having up to seven carbon atoms, phenyl, haloalkyl or aminoalkyl wherein at least two carbon atoms separate the halogen or nitrogen atom from the benzene ring, hydrocarbonoxy, or halohydrocarbonoxy wherein at least two carbon atoms separate the halogen and oxygen atoms; and each Q^2 is independently hydrogen, halogen, primary or secondary lower alkyl, phenyl, haloalkyl, hydrocarbonoxy or halohydrocarbonoxy as defined for Q^1.

5. The composition of Claim 1, in which the polyphenylene ether is poly(2,6-dimethyl-1,4-phenylene ether).

6. The composition of Claim 5, in which the poly(2,6-dimethyl-1,4-phenylene ether) has an intrinsic viscosity of about 0.40 to 0.5 deciliters per gram in choroform at 25°C.

7. The composition of Claim 1, in which the polyphenylene ether is poly(2,6-dimethyl-co-2,3,6-trimethyl-1,4-phenylene ether).

8. The composition of Claim 1, in which component (c) has a weight average molecular weight of at least 20,000, as determined by gel permeation chromatography.

9. The composition of Claim 1, in which component (c) has an average bromine substitution per aromatic nucleus of from 1 to 3.

10. The composition of Claim 1, in which component (c) is essentially a tribrominated polystyrene.

11. The composition of Claim 1, in which component (c) has been prepared by reacting polystyrene with bromine chloride in a solvent, in the presence of a Lewis acid bromination catalyst.

12. An article molded from the composition of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 86/02121

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

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

IPC^4: C 08 L 71/04; C 08 L 25/08; C 08 K 3/22; C 08 K 5/03; // (C 08 L 71/04,25:08,25:18) (C 08 L 25:08,71:04,25:18)

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 08 K; C 08 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	GB, A, 2076831 (GENERAL ELECTRIC) 9 December 1981, see claims 1,9-10 cited in the application --	1-3
X	JP, A, 60.90256 (MITSUBISHI GAS) 21 May 1985, see page 409, table 2; page 410, table 3 cited in the application ---------	1-3

* Special categories of cited documents: [10]

"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

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"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

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IV. CERTIFICATION

Date of the Actual Completion of the International Search 14th January 1987	Date of Mailing of this International Search Report 12 FEV. 1987
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer M. VAN MOL

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 86/02121 (SA 14955)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 26/01/87

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A- 2076831	09/12/81	FR-A,B	2483444	04/12/81
		NL-A-	8102633	16/12/81
		JP-A-	57021444	04/02/82
		DE-A-	3121067	18/03/82
		AU-A-	7119081	03/12/81
		AU-B-	544120	16/05/85
JP-A-60090256	21/05/85	None		

For more details about this annex :
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