



US005124404A

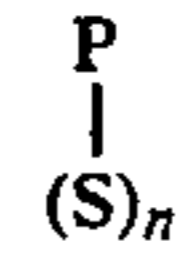
United States Patent [19][11] **Patent Number:** **5,124,404**

Atwell et al.

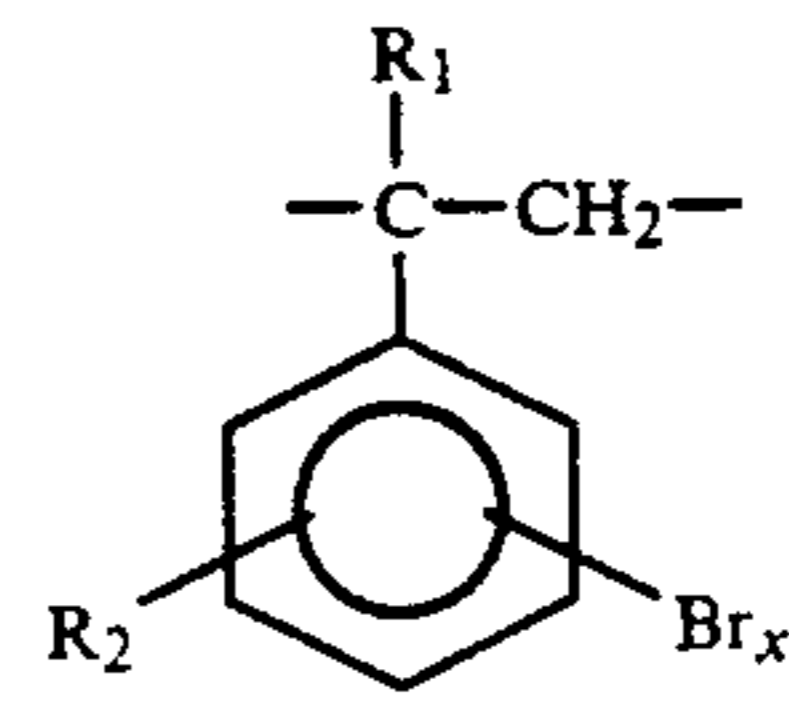
[45] **Date of Patent:** **Jun. 23, 1992**[54] **FLAME RETARDANT POLYPROPYLENE MOLDING COMPOSITIONS**[75] **Inventors:** **Ray W. Atwell**, W. Lafayette; **Donna L. Collison**; **Nicolai A. Favstritsky**, both of Lafayette; **Harry A. Hodgen**, Battle Ground; **Enrico J. Termine**, Lafayette, all of Ind.[73] **Assignee:** **Great Lakes Chemical Corp.**, W. Lafayette, Ind.[21] **Appl. No.:** **570,406**[22] **Filed:** **Aug. 21, 1990**[51] **Int. Cl.⁵** **C08L 51/06**[52] **U.S. Cl.** **525/72; 252/609**[58] **Field of Search** **525/302, 72; 252/609**[56] **References Cited****U.S. PATENT DOCUMENTS**3,458,597 7/1969 Jabloner 260/887
4,279,808 7/1981 Hornbaker et al. 260/45.75*Primary Examiner*—Melvyn I. Marquis*Assistant Examiner*—D. E. Aylward*Attorney, Agent, or Firm*—Woodard, Emhardt, Naughton, Moriarty & McNett[57] **ABSTRACT**

Described are polypropylene molding compositions

which have surprisingly good physical properties in combination with flame retardancy, which include copolymers represented by the formula:



wherein n is > 1, P is isotactic or syndiotactic polypropylene, and S is a grafted side chain having brominated monomeric units of the formula:

wherein x = 1 to 4, R₁ is H or CH₃, and R₂ is H or a C₁₋₄ lower alkyl group. Polymer blends including such graft copolymers and methods for making such flame retardant polymer compositions are also described.**14 Claims, No Drawings**

FLAME RETARDANT POLYPROPYLENE MOLDING COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention resides in the field of flame retardant polymers. More particularly, it relates to flame retardant polymer molding compositions which include graft copolymers of isotactic or syndiotactic polypropylene and brominated vinyl aromatics such as brominated styrenes.

2. Description of the Prior Art

By way of background, polypropylene has proven to be one of the most useful and versatile polymers. Its physical properties make it ideal for many applications including molded articles, spun fibers, hot melt adhesives and many others. These properties include, for instance, good surface appearance and solvent and stain resistance, and low moisture absorption. However, polypropylene does not possess adequate flame retardancy for certain applications. In view of its other desirable physical properties, it has naturally been a matter of great interest to provide polypropylene compositions with greater flame retardancy.

Improvement of flame retardancy has relied on modifications to polypropylene, or on additives for the polypropylene, but disadvantages have been associated with both approaches. Although a vast number of modified polypropylene compositions have been described or theorized in the prior art, few if any suitable flame retardant polypropylene derivatives have been identified. Similarly, numerous additives for increasing the flame retardancy of polypropylene have been studied and some are commercially available. Nonetheless, there is at present no commercially available flame retardant additive for polypropylene which provides adequate retention of polypropylene's physical properties, and demonstrates high thermal stability, non-migration of additive to the surface, and absence of solids at processing temperatures. The present invention contemplates a modification of polypropylene which yields a composition that retains the desirable physical properties of polypropylene, and avoids the disadvantages of alternate approaches.

In particular, the modified polypropylene of the invention avoids the frequently encountered migration or "bloom" of inert additive-type flame retardants to the surface of molded articles. Such bloom leads to unsightly surface discoloration on articles molded from the polypropylene and thereby effectively limits the amount of additive which can be used. Further, these inert additives frequently remain solid at processing temperatures, and can damage or foul processing equipment. For example, inert additives remaining solid at processing temperatures are known to cause problems by clogging spinnerettes used in equipment for producing spun fibers. This type of equipment fouling not only reduces the efficiency of processing but can also necessitate the costly refurbishment or premature replacement of equipment.

The applicants' preferred modified polypropylenes also avoid many other problems encountered in the prior art by having only low levels of unreacted styrene monomer, typically less than 1% by weight. For example, by this aspect the applicants' invention provides a vehicle to avoid monomer juicing problems known to occur in prior art graft modified compositions. It is also

significant that the compositions of the present invention can be efficiently processed without the release of excessive volatile monomer into the surrounding environment, which can be hazardous to those working with or near the materials. The prior art has failed to appreciate these substantial advantages of the compositions of the present invention.

As noted above, known flame retardant additives for polypropylene have recognized drawbacks. One such additive is hydrated alumina, which retards flame by releasing water under fire conditions. However, high loadings of hydrated alumina are necessary to give desired efficacy, and this results in poor physical properties of the polypropylene and articles molded therefrom. Among other defects, this results in undesirable changes in physical properties such as excessive stiffness, a reduction in tensile elongation, an increase in specific gravity, and a loss of "living hinge" capability.

Certain other available additives remain solid at normal polypropylene processing temperatures and thus complicate processing. Such additives include, for example, a bisimide-containing aliphatic bromine additive known as BN-451 from Ethyl Corp. of Sayreville, New Jersey, and a ring brominated polystyrene additive known as Pyro-Chek 68PB from Ferro Corp. of Cleveland, Ohio. The latter use of ring brominated polystyrene as an additive to polypropylene, rather than as a graft onto polypropylene, is a particularly clear demonstration of the failure of the prior art to recognize the present invention. Other available additives, such as decabromodiphenyl oxide, not only remain solid at processing temperatures but also are known to rise or "bloom" to the surface of molded articles. In U.S. Pat. No. 3,474,067, issued to Praetzel et al. on Oct. 21, 1969, there is described the use of ungrafted halogenated polystyrene homopolymer as a flame retardant additive for polyolefins in general, including polypropylene.

Aside from these inert additives, reports exist in the literature of attempts to chemically bond or graft flame retardants to polypropylene. To the applicants' knowledge, none of these techniques has been commercialized. For instance, M. Hartmann, et al., *Z. Chem.*, 20(4), 146-7 (1980), report preparing graft copolymers of atactic polypropylene and four respective vinylphosphonic acid derivatives. Two of the four copolymers prepared were reported as self extinguishing when containing greater than 3% by weight phosphorous. P. Citovicky et al., *Thermochim. Acta.* 93, 171-4 (1985), disclose a two-step procedure in which glycidyl methacrylate was grafted to isotactic polypropylene followed by reaction with various flame retardants including bromoacetic acid, 3,3',5,5'-tetrabromo-2,2'-dihydroxybiphenyl, dichloroacetic acid, or phenyldihydrogen phosphate. The copolymer reacted with phenyldihydrogen phosphate gave the highest limiting oxygen index value and was also reported the most thermally stable. In general, this technique is not particularly advantageous since it requires two steps and the flame retardant must be a functionalized molecule capable of reaction with an epoxide.

B. J. Hill et al., *Comm. Eur. Communities* [ReP.-]EUR, EUR 6718 (1980), report irradiation grafting of bis(2-chloroethyl)vinylphosphonate to polyester and polypropylene fabrics to render them self-extinguishing. The authors report that the bis(2-chloroethyl)vinylphosphonate had poor reactivity toward the fabrics. Comonomers were therefore required which in some

instances diminished flame retardancy and/or stiffened the fabrics.

K. Nakatsuka et al., Japan JP 44/3965 (Feb. 19, 1969), report air oxidizing polypropylene at elevated temperatures to introduce peroxy groups to the polymer followed by graft polymerization with $\text{CH}_2\text{CClCO}_2\text{Me}$. The product was reported to be self-extinguishing.

Outside of the field of flame retardancy, various modifications to polyolefins have been proposed. For example, U.S. Pat. No. 4,179,401, issued to Garnett et al. in 1979, relates to a process for producing a heterogenous catalyst for the hydrogenation, hydroformylation, isomerization, cracking or dehydrogenation of organic molecules. The Garnett process comprises the steps of radiation grafting a monomer having an alpha-unsaturated bond to a metal or an organic polymer and complexing a nitrogen, halogen, or phosphorous containing group to the monomer. The Garnett et al. patent lists many possible polymer/monomer combinations. Identified polymer substrates included polyvinyl compounds, polyolefins, polyvinylidenes, polysiloxanes, polydienes, polyethers, polyimides, polysulphones, polyesters, polyamides, polyurethanes, polycarbonates and polyureas. Listed as possible monomers for use in the described process were p-nitrostyrene, p-amino styrene, p-chlorostyrene, vinylidiphenylphosphine, cis-bis (1,2-diphenylphosphino) ethylene, triallylphosphine, divinylphenylphosphine and many more.

Similarly, U.S. Pat. No. 3,177,270, issued to Jones et al. in 1965, describes a method for modifying polyethylene and other substrates for the purpose of improving tensile strength, elongation and/or flexural modulus. The Jones et al. patent specifically described the preparation of ethylene polymer modified with styrene, a styrene/acrylonitrile mixture, dichlorostyrene or a mixture of isomeric vinyltoluenes. The Jones et al. patent additionally lists other possible polymeric substrates for use in the described method as including polypropylene, polyisobutylene, polybutene, and copolymers of ethylene and propylene, ethylene and butene, ethylene and styrene, ethylene and vinyl acetate, and ethylene and methyl methacrylate. Possible graft monomers are listed as including styrene, vinyltoluene, vinylxylene, ethylvinylbenzene, isopropyl styrene, para-tert-butyl styrene, dichlorostyrene, bromostyrene, fluorostyrene, or mixtures thereof with acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile, methyl methacrylate or maleic anhydride.

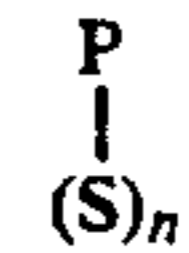
In U.S. Pat. No. 4,279,808, issued to Hornbaker et al. on Jul. 21, 1981, there is described a method for the preparation of polybromostyrene resin by the addition polymerization of nuclear brominated styrene. The Hornbaker et al. patent is limited to the addition polymerization of bromostyrene in the presence of specified rubbery polymers, namely SBR rubber (butadiene-styrene copolymers), EPR rubber (ethylenepropylene copolymers), EPDM rubber (i.e. terpolymers of ethylene, propylene and a diene monomer), polyisoprene rubber (e.g. cis 1,4 polyisoprene and trans-1,4-polyisoprene), Neoprene (i.e. polymers and copolymers of 2-chloro-1,3-butadiene), cis-1,4-polybutadiene, and polybutadienes having mixed structures (e.g. cis-1,4; trans-1,4 and 1,2 structures), with the polybutadienes being particularly preferred.

As is evident from the foregoing, past efforts to provide a polypropylene composition with improved flame retardancy have not been fully satisfactory. Available inert flameproofing additives have exhibited drawbacks

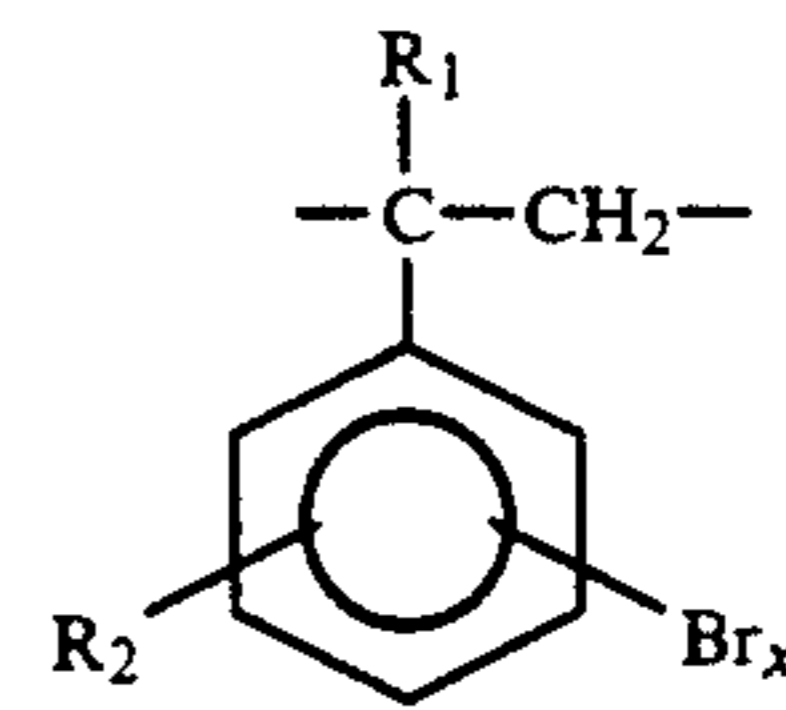
such as bloom and interference with desired physical properties. Additionally, polypropylene materials have not been provided with grafted fire retardants which perform as well as the present inventive compositions. Accordingly, there has remained a need for fire retardant polypropylene compositions demonstrating good physical properties, and the applicants' invention addresses this need.

SUMMARY OF THE INVENTION

Accordingly, a first preferred embodiment of this invention provides a flame retardant graft copolymer composition comprising:



in which n is an integer > 1, P is a moldable polypropylene, and S is a side chain grafted to the polypropylene and having brominated monomeric units of the formula:



wherein $x = 1$ to 4 , R_1 is H or CH_3 , and R_2 is H or a C_{1-4} lower alkyl group. In an alternate embodiment, the composition additionally includes a homopolymer of the brominated monomeric units.

Another preferred embodiment of this invention provides a flame retardant polymer composition comprising a blend of (i) moldable polypropylene, and (ii) a polymer composition including a graft copolymer according to the first embodiment above and constituted about 10% to about 60% bromine by weight. Such a blend can be prepared by diluting or "letting down" the bromine-concentrated polymer composition (ii) with a desired amount of polypropylene (i). After let down, the blend preferably comprises about 1% to about 20% bromine by weight of the blend.

It is an object of this invention is to provide flame retardant polypropylene-based molding polymer compositions which retain a desirable balance of physical properties, and which do not require flame retardant synergists.

Further objects include the provision of a flame retardant polypropylene molding composition which is characterized by high thermal stability, an absence of abrasive solids, a glossy surface appearance, an inherent whiteness, living hinge properties, and an immunity to water extraction.

Additional objects and advantages will be apparent from the description which follows.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

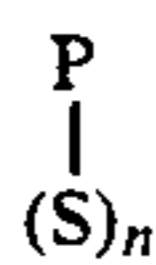
For the purposes of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments of the invention and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alter-

ations, further modifications and applications of the principles of the invention as described herein being contemplated as would normally occur to one skilled in the art to which the invention relates.

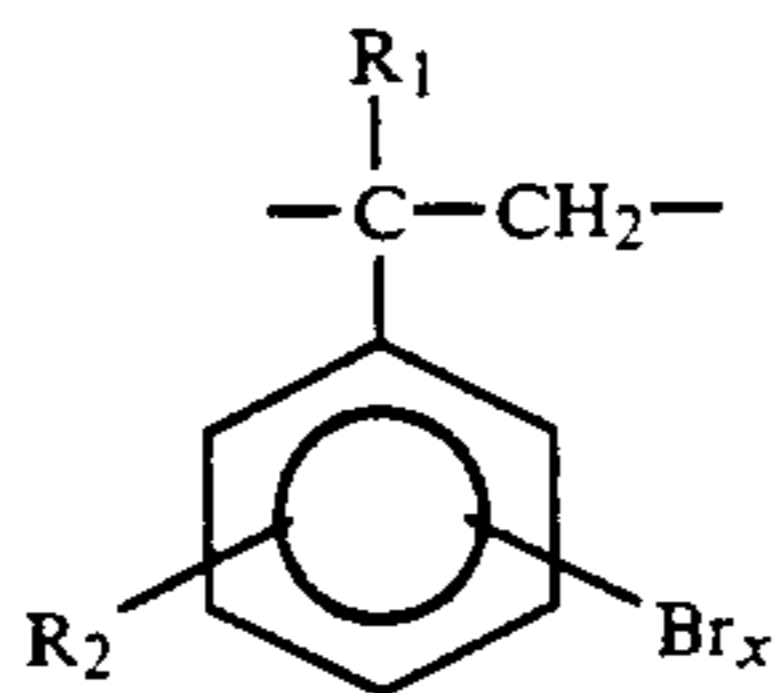
The present invention provides molding compositions which have physical properties comparable to that of polypropylene, but which have improved flame retardancy. In the broadest sense, isotactic or syndiotactic polypropylene is modified by grafting a ring-brominated vinyl aromatic onto the polypropylene. As used herein, the term polypropylene as relates to this invention refers to moldable compositions, and specifically to isotactic or syndiotactic polypropylene.

The presence of the bromine contributes to the flame retardancy of the resulting polymer. In contrast to the prior art, a significant portion of the bromine present in the compositions of the present invention is grafted onto, i.e. attached to, the polypropylene through the monomeric unit. In addition, it is contemplated that the final compositions may also include bromine in the form of homopolymers of the monomer used in grafting the polypropylene. Although not to be considered limiting of the present invention, it is believed that the compatibility of the grafted polypropylene and the homopolymer contributes to the desirable physical properties of the resulting composition.

In accordance with the above discussion, one embodiment of this invention includes a flame retardant polymer composition comprising a graft copolymer represented by the formula:



in which n is an integer > 1 , P is isotactic or syndiotactic polypropylene, and S is a side chain grafted to the polypropylene and having monomeric units of the formula:



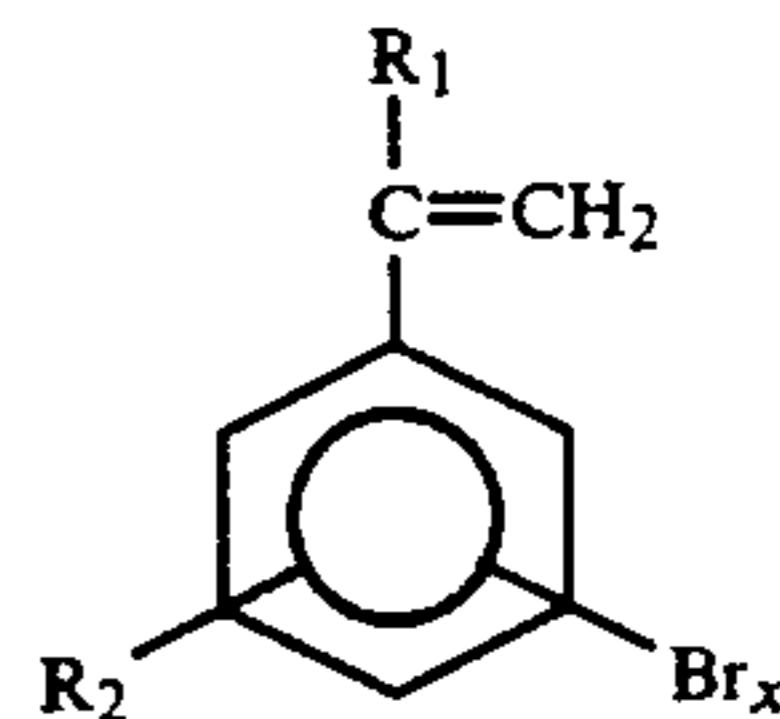
wherein $x = 1$ to 4 , R_1 is H or CH_3 , and R_2 is H or a C_{1-4} lower alkyl group.

The form of the polypropylene used in the present invention is not critical so long as it undergoes suitable graft polymerization to yield the indicated molding compositions. Thus the polypropylene base in the graft copolymer can include crystalline polypropylene homopolymer in isotactic or syndiotactic form. Further, polypropylene materials with melt indices of about 0.1 to about 200 grams per 10 minutes (as measured by ASTM D-1238) can be employed. The preferred range of melt index is from 1 to 50 grams per 10 minutes.

The polypropylene is graft polymerized with a ring-brominated vinyl aromatic which is also optionally alpha- or ring-substituted with one or more aliphatic groups including lower alkyl groups such as methyl, ethyl, and propyl and butyl isomers. This monomer is preferably a styrene having 1 to 4 ring-substituted bromines. However, it will be appreciated that monovinyl aromatics, including for instance styrenes which are alpha- or ring-substituted with one or more lower ali-

phatic groups as described herein, function similarly to styrene in grafting procedures and are accordingly also within the scope of this invention. In this vein, methyl is a preferred optional alpha-substituted alkyl group and C_{1-4} lower alkyls are preferred optional ring-substituted alkyl groups.

Accordingly, preferred brominated monomers suitable for the graft polymerization process have the formula:



wherein $x = 1$ to 4 , R_1 is H or CH_3 , and R_2 is H or a C_{1-4} lower alkyl group.

In accordance with this formula the preferred styrene monomer has 1 to 4 bromines per styrene, or can also include mixtures containing these mono-, di-, tri-, and/or tetrabromostyrenes. Pentabromostyrene is not a preferred styrene monomer as in the applicants' work it has failed to efficiently graft to polypropylene either alone or in combination with a lesser-brominated styrene comonomer. It is desirable that the monomer material used for the graft polymerization contain a high percentage of bromine while remaining liquid at room temperature (about $25^\circ C.$). Mixtures of styrenes may accordingly be used which are liquid at room temperature and which have varying degrees of bromination to achieve a high percentage of bromine in the monomer material.

In another aspect, it is preferred that the stated levels of bromine be achieved with at least about 85% of the brominated monomeric units being di-, tri- or tetrabromo units or mixtures thereof, and more preferably with at least about 80% of the brominated monomeric units being dibromo units. The most preferred monomer is dibromostyrene. In commercial form dibromostyrene commonly includes minor levels of mono- and tribromostyrene. For example, the applicants have used dibromostyrene available from Great Lakes Chemical Corporation of West Lafayette, Indiana, which normally contains about 15% monobromostyrene and about 3% tribromostyrene by weight. The preferred styrene monomer can also contain storage stabilizers as known and used in this field to inhibit premature polymerization. As examples, these commonly include phenols and compounds of sulfur, nitrogen and phosphorous.

The ring-brominated vinyl aromatic is grafted to the polypropylene base using suitable known graft polymerization techniques which may be performed, for example, in solution, suspension, emulsion or bulk procedures. Grafting techniques include for instance irradiation, peroxidation by exposure to oxygen at elevated temperatures, and abstraction of protons by free radical initiators. Among these, the latter technique is preferred, with appropriate free radical initiators including dicumylperoxide, benzoylperoxide, t-butylperbenzoate, 2,2'-azobis(isobutyronitrile), cumenehydroperoxide or the like.

In a typical grafting procedure, the free radical initiator is dissolved in the brominated monomer at suitable

levels, generally from about 0.1% to about 5% and preferably from about 1% to about 3% on weight of the monomer. The resulting solution is then added to agitated molten polypropylene. In this regard, the grafting is preferably performed in a kneading type mixer such as a Banbury mixer, or in an extruder or a two-roll mill, although other suitable mixers known in the art can also be used.

Additionally, the grafting is carried out at a suitable pressure and elevated temperature and for a duration sufficient to yield the desired end product. Generally, the temperature will be sufficiently high to reduce the viscosity of the molten polypropylene and to ensure thorough mixing. Moreover, where free radical initiators are used, this temperature will be high enough to promote decomposition of the initiator resulting in rapid polymerization of the monomer. In any case, preferred temperatures for the grafting procedure are from about 120° C. to about 230° C., with more preferred temperatures being about 170° C. to about 200° C.

The grafting proceeds readily at atmospheric pressure as well as at the elevated pressures encountered in commonly used plastics processing equipment. The duration of the grafting procedure will depend upon the temperature as well as the grafting technique used. In free radical initiated grafting, the duration will also depend upon the chosen initiator and the efficiency of mixing. Generally, however, durations ranging from about 1 second to several hours can be used, with about 10 to about 300 seconds resulting in an efficient polymerization and thus being preferred.

Graft polymerization will typically result in both grafted polypropylene and homopolymer of the selected monomer. It has been found that the grafted polypropylene and any homopolymer present remain well intermixed, even during processing. The homopolymer could alternatively be removed, but this is not necessary and the preferred composition therefore includes both grafted polypropylene and homopolymer.

The present invention provides polymer compositions having a flame retarding amount of bromine, about 1 weight % or more, based on the weight of the overall composition. This bromine may be present either in the grafted polypropylene or in a homopolymer mixed with the grafted polypropylene. In any event, however, the grafted polypropylene copolymer includes at least about 0.5%, and more preferably at least about 1%, bromine by weight. As processed (e.g. molded or spun), the preferred flame retardant polymer compositions of the invention will generally include about 1% to about 20% bromine by weight of the composition, and more preferably about 3 to about 15% bromine by weight.

In another preferred embodiment of the invention, a bromine-concentrated polymer composition is provided having about 10% to about 60% bromine by weight, or more preferably about 30% to about 50% bromine by weight, of the overall product. In this embodiment, the grafted polypropylene copolymer preferably includes at least about 5% bromine by weight for the broad range, and at least about 15% for the more preferred range. This composition can thereafter be let down with polypropylene prior to processing to yield a resulting composition having an appropriate level within the 1% to 20% or more preferred 3% to 15% bromine range. The advantage in this approach is the maximization of physical strength properties by the introduction of

polypropylene into the composition which has not been exposed to the harsh conditions of the grafting process.

A certain amount of bromine may also be present as a part of unreacted monomer, but this form is not preferred and the amount of unreacted monomer is desired to be relatively low. This will prevent or minimize juicing, i.e., migration of the monomer to the surface. The amount of unreacted monomer is preferably at most about 3% by weight, and more preferably at most about 1% by weight, of the overall composition. These low levels are generally achieved in the preferred products without the need for further processing steps. However, when desired the unreacted monomer can be removed, for example, by placing the graft polymerization products under vacuum.

The let down blends and other polymer compositions of the applicants' invention have demonstrated excellent flame retarding properties as, for instance, the specific Examples demonstrate. In addition, the compositions of the invention, particularly the let down blends, have demonstrated excellent physical properties. This can be seen for example from the high values reported in Table 2 for impact strength and percent elongation. The combination of improved flame retardancy and desirable physical properties, especially without bloom, juicing, etc. found in prior art approaches, provide a significant and unexpected advantage, and highlight the magnitude of the applicants' discoveries.

Additional materials which do not significantly interfere with the grafting procedure or the resulting products can also be used as known in the art or determined by routine experimentation. For instance, reactive additives such as chain transfer agents can be dissolved into the brominated monomer prior to grafting to control the molecular weight of the brominated polymer content of the graft procedure. Alkyl halides and mercaptans, particularly 1-dodecanethiol, for example, are suitable chain transfer agents for limiting the extent of styrene polymerization and thus the molecular weight of the styrene polymer chains. Loadings from 0.1% to 5% on weight of the monomer may be used, with 0.5% to 3% being typical. As will be understood, the product of the graft polymerization will normally contain brominated styrene polymer grafted to the polypropylene as well as brominated styrene homopolymer resulting from separate polymerization of the monomer. The chain transfer agent can thus be used to regulate the molecular weight of each.

Other reactive unsaturated comonomers can also be included during the grafting process to modify the properties of the resultant polymer composition. These can include for example maleic anhydride, styrene, chloromethylstyrene, acrylonitrile, methylmethacrylate, acrylic acid, butene, butadiene, acrylamide and many others as known in the art. Modifications which can be achieved by addition of other materials during the grafting process include alterations in color, clarity, lubricity, dyability, melt viscosity, softening point, thermal stability, ultraviolet stability, viscoelastic behavior, polarity, biodegradability, static charge dissipation, strength and stiffness.

Nonreactive materials can also be included in the grafting procedure to modify product properties. As examples, antioxidants, ultraviolet absorbers, antistatic agents, pigments, dyes, nucleating agents, fillers, slip agents, lubricants, antiblocking agents, plasticizers, and/or antimicrobials can be included. These materials can be incorporated into the polypropylene prior to or dur-

ing the grafting process. Alternatively, these materials can be added in a separate compounding step which provides the advantage of avoiding possible interference by these additives with the grafting chemistry.

Additional flame retardants (aside from the brominated styrene) can also be included in the graft polymerization product when desired to improve efficiency and lower costs. These may be reactive flame retardants such as bis(2-chloroethyl)vinylphosphonate or acrylic acid esters of halogenated alcohols, or inert flame retardants such as antimony oxide, triphenylphosphate, brominated diphenyl oxides, tetrabromobisphenol A or its derivatives or hexabromocyclododecane.

The polypropylene resins of the present invention are reduced in flammability. In addition, these compositions possess a unique combination of desirable properties not attainable with other additives. They are particularly useful in the production of molded or extruded articles such as electrical appliance cabinets or wire coatings that require reduced flammability.

The invention will be further described with reference to the following specific Examples. It will be understood that these Examples are illustrative and not restrictive in nature. In the following Examples, percents indicated are percents by weight unless indicated otherwise.

EXAMPLE 1

Dibromostyrene Grafted Onto Polypropylene

63 g of dicumylperoxide were dissolved into 3157 g of dibromostyrene (also containing 15% by weight monobromo- and 3% by weight tribromostyrene) from Great Lakes Chemical Corporation of West Lafayette, Indiana. In a continuous process the monomer was metered at 3.2 lbs/hr to a Werner & Pfleiderer twin screw extruder while simultaneously feeding polypropylene homopolymer (AMOCO 10-5219) at 17.6 lbs/hr. Temperature in the extruder was graduated from 170° C. in Zone 1 to 185° C. in Zone 5, and screw speed was 160 revolutions per minute (rpm's). The molten product was stranded into a water bath and was then granulated. The graft copolymer was found to contain 8.4% bromine and had a residual monomer content of 0.52%.

EXAMPLE 2

A second graft copolymer was prepared using the procedure described in Example 1. A slightly faster rate of dibromostyrene addition was used, however, so that the product this time contained 9.1% bromine and 0.68% residual monomer.

EXAMPLE 3

Concentrated Dibromostyrene/Polypropylene Graft Copolymer

24 g of dicumylperoxide were dissolved into 1212 g of Great Lakes Dibromostyrene. In a batch process, 250 g of the monomer plus peroxide were added to 105 g of molten polypropylene homopolymer (AMOCO 10-5219) in a Brabender Prep Center (a Banbury-type mixer). Bowl temperature was maintained at 180° C. while mixing at 50 rpm's as the monomer was being added over a 10 minute period. Following the addition of the last of the monomer, the mixture was held an additional 5 minutes at 180° C. The product was emptied from the bowl, cooled to room temperature and granulated. The graft concentrate was found to contain

40.5% bromine with a residual monomer content of 0.57%.

EXAMPLE 4

Tribromostyrene Grafted to Polypropylene

A mixture of 11.1 g of powdered tribromostyrene and 0.22 g of dicumylperoxide were dry blended. Separately, 48.9 g of polypropylene (AMOCO 10-5219) were melted in a small Brabender Plasticorder mixer at 180° C. and 60 rpm's, and the tribromostyrene/peroxide mixture was spooned in over a 2 minute period. The resulting graft copolymer was held an additional 5 minutes at 180° C./60 rpm's before cooling and granulating. The product was found to contain 10.6% bromine with a residual monomer content of 0.06%.

EXAMPLE 5

Comparative Example

Attempt to Graft Pentabromostyrene to Polypropylene

A mixture of 9.9 g of powdered pentabromostyrene and 0.20 g dicumylperoxide were dry blended. Separately, 50.1 g of polypropylene (AMOCO 10-5219) were melted in a small Brabender Plasticorder mixer. Using the same conditions as in Example 3, the pentabromostyrene plus peroxide mixture was added. On removing the product from the bowl, powdery white residue was observed on the surface of the bowl and on areas of the product. The product was found to contain 13.1% bromine and 11.1% residual pentabromostyrene monomer, thus indicating that 67% of the monomer charged failed to polymerize.

EXAMPLE 6

Comparative Example

Attempt to Graft Pentabromostyrene to Polypropylene

8.3 g of powdered pentabromostyrene were dry blended with 0.16 g t-butylperbenzoate. The mixture was added in a single dose to 41.7 g polypropylene (AMOCO 10-5219) which was mixing at 190° C./60 rpm's in a Brabender Plasticorder. After 5 minutes at 190° C. the product was removed and granulated. The product was found to contain 12.6% bromine and 10.7% residual pentabromostyrene monomer, and thus 64% of the pentabromostyrene failed to polymerize.

EXAMPLE 7

Comparative Example

Attempt to Co-graft Pentabromostyrene and Dibromostyrene

A slurry of 4.8 g of pentabromostyrene, 4.8 g of dibromostyrene and 0.19 g of dicumylperoxide was prepared. Using the conditions from Example 6, the slurry was added to 40.4 g of polypropylene (AMOCO 10-5219). The product was found to contain 11.9% bromine and 5.3% residual pentabromostyrene monomer. It also contained 1.6% residual mono- and dibromostyrene. Thus, based upon the amount of monomers added, 55% of the pentabromostyrene and 17% of the mono- and dibromostyrene failed to react.

Discussion of Examples 1 to 7 (Graft Preparation)

Example 1 illustrates a continuous grafting process in which only the final needed amount or "flame retarding quantity" of dibromostyrene was added to the polypropylene. The composition was not blended further with

11

any additional base resin. This demonstrated that dibromostyrene can be used to prepare a flame retardant composition directly without leaving unacceptably high levels of residual monomer. Example 2 is very similar to Example 1, with a higher level of bromine being introduced.

In Example 3, a concentrate was prepared using a batch process, indicating that a product with a high bromine content can be prepared which also has a low residual monomer. Example 4 demonstrates that tribromostyrene can be substituted for dibromostyrene.

Example 5 shows that conditions which worked well for dibromo- and tribromostyrene left large amounts of unpolymerized pentabromostyrene in the product. Further, the unpolymerized pentabromostyrene is incompatible with the polypropylene and migrates to the surface as a white powder. In Example 6, most of the pentabromostyrene again failed to polymerize even in the presence of a qualified alternate initiator and at 10° C. higher temperature. In Example 7, pentabromostyrene is shown not to be useful even when mixed with the more reactive dibromostyrene. Furthermore, the presence of pentabromostyrene inhibits polymerization of the lower brominated species, resulting in high levels of unreacted mono- and dibromostyrene.

EXAMPLE 8

The graft copolymer from Example 1 was molded into test specimens using a Newbury Injection Molding Machine (Model HI-30 RS, Newbury Industries, Inc., Newbury, OH). Molding conditions are shown in Table 1:

TABLE 1

Conditions for Injection Molding	
Injection Pressure, psi	500
Cycle time, sec.	30
Rear Temperature, °F.	370
Front Temperature, °F.	380
Mold Temperature, °F.	75
Screw Speed, rpm	100
Injection Time, sec	10

The molded specimens were uniformly white with a very glossy surface.

EXAMPLE 9

The graft copolymer concentrate from Example 3 was dry blended with base polypropylene at a ratio of 700 g of graft concentrate per 1500g of polypropylene (AMOCO 10-5219). The dry blend was then melt blended by passing it through a 30 mm twin screw extruder (Werner & Pfleiderer Model ZSK 30) at 180° C. The let down mixture was found to contain 12.9% bromine and 0.25% residual monomer.

EXAMPLE 10

The let down mixture from Example 9 was molded into test specimens using the procedures and conditions shown in Example 8. The molded specimens were uniformly white with a very glossy surface.

EXAMPLE 11

Comparative Example

390 g of polypropylene (AMOCO 10-5219) were dry blended with 110 g of polydibromostyrene homopolymer containing 58.5% bromine. The mixture was melt

12

blended as in Example 9 to obtain a composition containing 12.9% bromine.

EXAMPLE 12

Comparative Example

The composition from Comparative Example 11 was molded into test specimens using the procedures and conditions shown in Example 8.

EXAMPLE 13

Comparative Example

Unmodified polypropylene (AMOCO 10-5219) was molded into test specimens using the procedures and conditions shown in Example 8.

EXAMPLE 14

The composition from Example 2 was molded into test specimens using the procedures and conditions shown in Example 8.

EXAMPLE 15

Injection molded test specimens from Example 10 were maintained at 75° C. to 80° C. for 53 days in a gravity oven. Surfaces remained perfectly glossy with no trace of bloom.

EXAMPLE 16

9.8 g of a molded specimen from Example 10 were dissolved in 279 g of boiling xylenes (Mallinckrodt #8664). The warm solution was added dropwise to 2 liters of vigorously stirring methanol. The precipitated polymer was removed by filtration and dried. Yield was 100%. A portion of the polymer (4.9 g)—now having greatly increased surface area—was treated with approximately 500 ml of methylene chloride in a Soxhlet Extractor for 6 hours. The methylene chloride solution was evaporated to dryness to obtain 0.94 g of solid which was found to contain 44.53% bromine. The polymer after extraction still contained 4.32% bromine, or 33% of the bromine present before extraction.

EXAMPLE 17

Comparative Example

9.7 g of molded specimens from Comparative Example 12 were dissolved, precipitated and extracted as described in Example 16. 0.749 g of extract were recovered which contained 52.1% bromine. The bromine content of the polymer after extraction was "none detected" with a detection limit of 0.2%. Before extraction (but after precipitation) it contained 12.19% bromine.

EXAMPLE 18

84.6 g of graft concentrate from Example 3 and 5.4 g atactic Polypropylene (diluent) were blended in a Brabender Plasticorder for 10 minutes at 190° C. A portion of the mixture was put into a test tube and placed in an oven at 190°-200° C. for 7 hours. The mixture was cooled, the glass broken away, and samples were taken from near the top and bottom. Bromine content near the top was 36.5%, and near the bottom it was 37.2%. Based on the materials added, the bromine content should have been 38.1%.

EXAMPLE 19

Comparative Example

The following were blended as in Example 18:
 21.6 g Polypropylene (AMOCO 10-5219)
 63.0 g Polydibromostyrene Homopolymer
 5.4 g atactic Polypropylene (diluent)

Part of the mixture was put into a test tube, heated and sampled as in Example 18. In contrast to the results in Example 18, bromine content near the top was 12.8% while it was 48.6% near the bottom. Calculated bromine content was 40.9% based on the materials charged.

EXAMPLE 20

Known graft polymerization procedures are used to graft Great Lakes Dibromostyrene to isotactic and syndiotactic polypropylene in amounts whereby the graft polymerization products comprise about 1% to about 60% by weight bromine.

EXAMPLE 21

The graft polymerization products of Example 20 having about 10% to about 60% by weight bromine are blended with polypropylene using known techniques to achieve bromine levels in the final blend ranging from about 1% to about 20% by weight bromine.

EXAMPLE 22

A 5×0.5×1/16 inch molded test strip from Example 10 was evaluated for living hinge behavior. The strip was folded in half and pinched to form a permanent crease. With one end held stationary, the other end was then brought around in a counter clockwise direction until the ends touched, followed by a 360 degree movement in the opposite direction until the ends touched again. This constituted one cycle. The procedure was repeated for 100 cycles. There was no obvious damage to the hinge; twisting the free end 90 degrees in either direction did not cause any tearing at the crease.

EXAMPLE 23

Physical properties were determined for several of the molded compositions. Results are shown in Table 2.

TABLE 2

	Physical Property Test Results			
	Compar. Ex. 13	Ex. 8	Ex. 10	Compar. Ex. 12
Flex. Strength, psi	6600	8290	7570	8000
Flex. Mod., psi × 10 ⁵	2.13	2.81	2.64	2.95
Tensile Strength, psi	5250	5660	5530	5300
Elong. @ Peak, %	8.4	6.8	7.1	3.6
Tensile Mod., psi × 10 ⁵	2.24	2.73	2.59	2.84
Izod Impact (Un-notched), ft. lbs./in.	21.7	5.9	17.9	8.5

EXAMPLE 24

Molded specimens were tested for flammability using the Underwriters Laboratories Standard UL-94 and the ASTM D-2863 Oxygen Index Test. Results are shown in Table 3:

TABLE 3

	Flammability Test Results				Comp Ex. 12
	Comp. Ex. 13	Ex. 8	Ex. 14	Ex. 10	
Bromine Content, %	0.0	8.4	9.1	12.9	12.9
UL-94, 1/16 inch	Fail	Fail	94V-2	94V-2	Fail
Oxygen Index, %O ₂	19.0	24.0	24.5	25.0	22.5

Discussion of Examples 8 to 24 (Utility)

The results in Table 2 show that the compositions of our invention retain a good balance of properties compared with the unmodified base resin. Strength properties and stiffness are increased while tensile elongations are slightly reduced. The material in Example 10—made from the graft concentrate—shows a higher level of toughness (as measured by impact strength) than the graft of Example 8.

The inherently white and glossy appearance of the molded specimens is a distinct advantage. It means that the graft copolymers will be easy to pigment to consistent color shades without the addition of whitening agents such as titanium dioxide that cause filler type problems which were described previously. The surface gloss is visually appealing, giving molded articles a finished appearance without any costly post-molding treatments.

Comparative Example 12 contains the same level of bromine as Example 10, but the brominated polystyrene is present only as an additive; none is grafted to the polypropylene. The starting brominated monomer in both cases was Great Lakes Dibromostyrene. In spite of the similarity in the structures of the flame retardants, the ungrafted polymer produces excessive stiffness in the blend which is very apparent in the low value for tensile elongation.

The flammability test results in Table 3 demonstrate that the compositions of our invention exhibit improved flame retardancy over the unmodified base resin. This is most easily quantified by the Oxygen Index values. Equally as important, note that the graft copolymers (Examples 8, 10, and 14) show a surprising improvement in efficiency compared with ungrafted brominated polystyrene that is simply mixed into the polypropylene. It is unexpected that the 9.1% bromine of Example 14 would perform so much better than the 12.9% of Comparative Example 12, especially in light of the fact that the starting monomer in both cases was Great Lakes Dibromostyrene.

In Example 16, 36% of the brominated styrene was not extractable using methylene chloride because the polymer was chemically grafted to the polypropylene. The ordinary blend in Comparative Example 17, on the other hand, was essentially stripped of all brominated polymer by the extraction. Similarly, the graft copolymer in Example 18 remained homogeneous in the melt, while the blend in Comparative Example 19 stratified on standing, with the dense brominated polymer concentrating near the bottom. These examples evidence that our invention is not just a mixture of polymers, but rather that a new composition has formed.

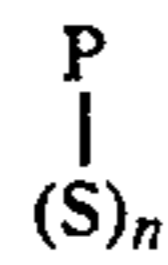
While the invention has been described in detail in the foregoing description and its specific Examples, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiments have been described and that all

15

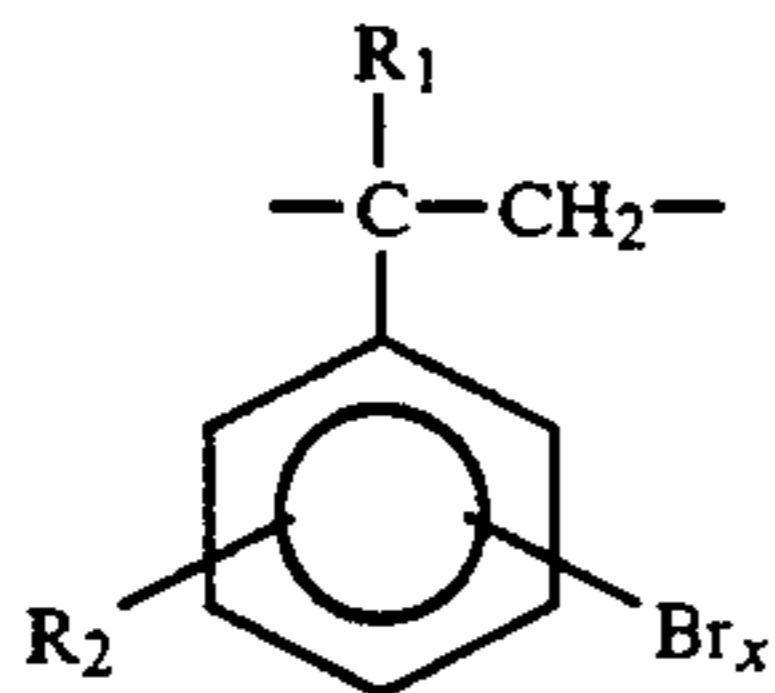
changes and modifications that come within the spirit of the invention are desired to be protected.

What is claimed is:

1. A flame retardant copolymer molding composition comprising:



wherein n is >1, P is isotactic or syndiotactic polypropylene, and S is a grafted side chain having brominated monomeric units of the formula:



wherein x=1 to 4, R₁ is H or CH₃, and R₂ is H or a C₁₋₄ lower alkyl group, said copolymer including at least bromine by weight of graft copolymer.

2. A flame retardant copolymer molding composition according to claim 1 comprising about 1% to about 60% by weight bromine.

3. A flame retardant copolymer molding composition according to claim 2 comprising about 1% to about 20% by weight bromine.

4. A flame retardant copolymer molding composition according to claim 3 comprising about 3% to about 15% by weight bromine.

5. A flame retardant copolymer molding composition according to claim 2 comprising about 10% to about 60% by weight bromine.

6. A flame retardant copolymer molding composition according to claim 5 comprising about 30% to about 50% by weight bromine.

7. A flame retardant copolymer molding composition according to claim 1 and containing at most about 3%

16

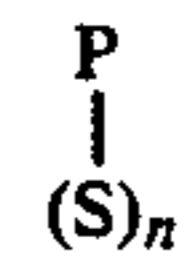
by weight of unreacted brominated monomer corresponding to the brominated monomeric units.

8. A flame retardant copolymer molding composition according to claim 7 and containing at most about 1% by weight of said unreacted brominated monomer.

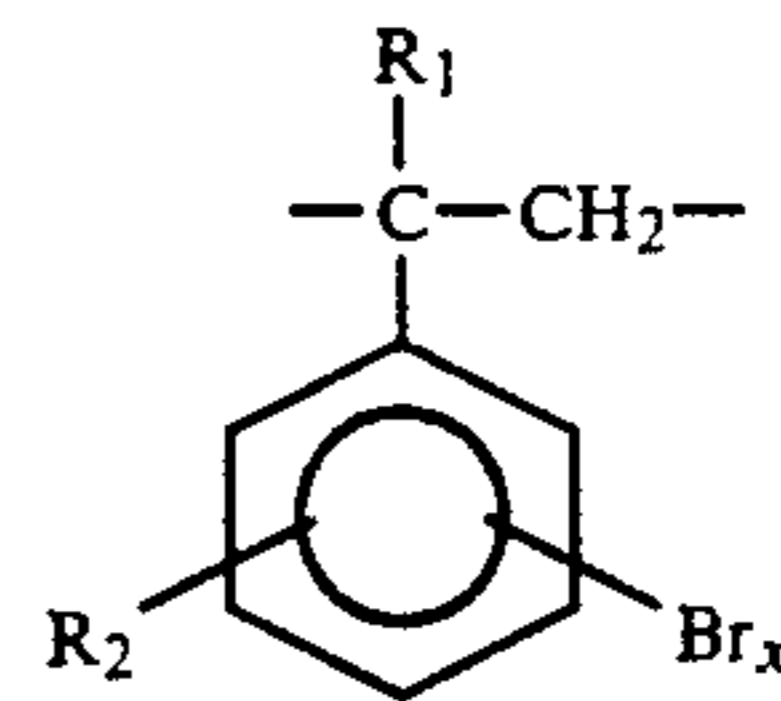
9. A flame retardant copolymer molding composition according to claim 1 in which R₁ and R₂ are each H.

10. A flame retardant copolymer molding composition according to claim 1 in which at least about 80% of said brominated monomeric units have formulas wherein x=2.

11. A molded article comprised substantially of the composition:



wherein n is >1, P is isotactic or syndiotactic polypropylene, and S is a grafted side chain having brominated monomeric units of the formula:



wherein x=1 to 4, R₁ is H or CH₃, and R₂ is H or a C₁₋₄ lower alkyl group, said graft copolymer including at least about 1% bromine by weight of graft copolymer.

12. The composition of claim 1 in which at least about 85% of said brominated monomeric units have formulas wherein x=2, 3 or 4.

13. The composition of claim 1 and which consists essentially of said polypropylene and said grafted side chains.

14. The composition of claim 13 in which at least about 85% of said brominated monomeric units have formulas wherein x=2, 3 or 4.

* * * * *

45

50

55

60

65

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,124,404

DATED : June 23, 1992

INVENTOR(S) : Ray W. Atwell, Donna L. Collison, Nicolai A.
Favstritsky, Harry A. Hodgen, Enrico J. Termine

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 1, line 53 change "Processing" to --processing--.

In Column 4, line 47 delete the word "is" following "invention".

In Column 12, line 50 add two spaces after "16."

In Column 15, line 24 add the words "about 1%" before bromine.

Signed and Sealed this

Twenty-sixth Day of October, 1993

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks