PCT

(54) Title: FLAME RETARDANT FOR STYRENE RESIN AND RESIN COMPOSITION COMPRISING THE SAME

(57) Abstract

A low volatility flame retardant for a styrene resin comprising an aromatic phosphate represented by formula (I) wherein $\underline{a}$, $\underline{b}$, and $\underline{c}$ each independently represent an integer of from 1 to 3; and R_1, R_2, and R_3 each independently represent a hydrogen atom or a halogen-free alkyl group having from 1 to 30 carbon atoms, which is not an isopropyl group, the total number of carbon atoms in the substituents represented by R_1, R_2 and R_3 being from 12 to 25 on an average in one molecule of said aromatic phosphate, provided that when said flame retardant comprises a plurality of aromatic phosphates having different substituents, the total number of carbon atoms in the substituents R_1, R_2 and R_3 of said flame retardant is represented by a number average in the whole of said flame retardant, which is the sum of the products of the weight fraction of respective aromatic phosphate and the total number of carbon atoms in the substituents in respective aromatic phosphate.

DESCRIPTION

FLAME RETARDANT FOR STYRENE RESIN AND
RESIN COMPOSITION COMPRISING THE SAME

Technical Field

The present invention relates to a low volatility
flame retardant for a styrene resin. More particularly, the
present invention relates to a low volatility flame retardant
for a styrene resin which forms no mold deposit even after a
prolonged continuous molding, and a resin composition
comprising such a flame retardant.

Background Art

Because of its excellent impact resistance in
addition to excellent moldability, a styrene resin has found
wide application in many fields such as automobile parts,
household appliance and OA (office automation) equipment
parts. However, the styrene resin has restricted usage due
to its flammability.

A known method for flame-retarding the styrene resin
is to incorporating a halogen, phosphorus or inorganic flame
retardant in the styrene resin. This method can attain flame
retardation to some extent. However, the use of a halogen
flame retardant disadvantageously causes environmental
hazard. The use of a phosphorus or inorganic flame retardant
is not satisfactory in the resulting impact strength, melt

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flowability and heat resistance. Further, a non-volatile

organic phosphorus compound can cause staining of mold, i.e.,

so-called mold deposit during molding, reducing the

productivity. The mold staining may be transferred to molded

5   products, causing stress crack thereof. Thus, the industrial

use is restricted.

As an approach for improving the volatility there is

disclosed a resin composition for laminate comprising a

phenolic resin and a specific monomeric alkyl-substituted

10   phosphate (JP-A-1-95149 (The term "JP-A" as used herein means

an "unexamined published Japanese patent application"), JP-A-

1-242633, JP-A-1-193328). The flame retardants disclosed in

these documents apply to thermosetting resins. Thus, these

flame retardants are not those for the styrene resin of the

15   present invention.

An antistatic agent comprising a sulfonate and a

phosphate such as dinonylphenyl phenylphosphate (JP-A-3-

64368) and a lubricant comprising a polyol ester and a

triaryl phosphate such as bisnonylphenyl phehylphosphate

20   (U.S. Patent 4,780,229) are disclosed. However, these

compounds disclosed in these documents are not flame

retardants and differ essentially from the present invention.

There have been known a resin composition comprising

a polycarbonate, an ABS resin, a halogenated phosphate and a

25   polytetrafluoroethylene (WO9106598), a resin composition

comprising a polycarbonate, an AAS resin, a phosphate and a

polytetrafluoroethylene (EP534297), a resin composition comprising a polycarbonate, an ABS resin, a phosphate and a polytetrafluoroethylene (DE4309142), a resin composition comprising a polycarbonate, an ABS resin, an aromatic phosphate and a metal salt of aromatic sulfinic acid (JP-A-6-299060), a resin composition comprising a polycarbonate, a polyester polycarbonate, an ABS resin, a phosphate and a polytetrafluoroethylene (EP482451), and a resin composition comprising a polycarbonate, an ABS resin, a phosphate and a polycarbonate-siloxane block copolymer (DE4016417). The phosphate to be incorporated in the foregoing polycarbonate resin composition comprises no phosphate having a specific substituent and thus exhibits a poor balance between non-volatility and flame retardance.

Further, there have been disclosed a flame retardant comprising a phosphate having a phenyl group, an isopropylphenyl group and a C_{4-12} alkyl-substituted phenyl group (JP-A-2-792 corresponding to EP324716), a flame retardant resin comprising a polyphenylene ether, a styrene resin and tris(isopropylphenyl)phosphate (JP-A-1-48844), and a functional fluid composition comprising a polystyrene, t-butylphenyl phenylphosphate and a polyol ester (USP4645615). The total number of carbon atoms in the substituents in the phosphate of these documents on the number average falls below 12 based on the definition in the present invention

described later. Thus, these compounds are insufficient in
non-volatility.

The expression "C_{x-y} alkyl" and the like used herein
means "alkyl having from x to y carbon atoms" and the like.

Further, there has been disclosed a flame retardant
resin composition comprising a phosphate wherein the
substituents R_1, R_2 and R_3 in formula (I) of the present
invention described later each represent an aromatic
hydrocarbon, such as tris(4-phenylphenyl)phosphate and
tris(benzylphenyl)phosphate (DE4016417, EP534297, EP534297).
The flame retardant comprising such a phosphate exhibits an
excellent heat resistance but a poor melt flowability and
flame retardance.

As approaches for flame-retarding the styrene resin
there have been disclosed a flame retardant resin composition
comprising a polyphenylene ether, a styrene resin, a metal
salt of phosphoric acid and a phosphate such as
tris(nonylphenyl)phosphate (JP-A-63-305161), a polyphenylene
ether resin composition comprising a polyphenylene ether and
a high molecular weight polyethylene as essential components,
and optionally a phosphate such as tris(nonylphenyl)phosphate
(EP550204), and a flame retardant resin composition
comprising an aromatic polycarbonate, an ABS resin, an AS
resin, a phosphate such as tris(nonylphenyl)phosphate, an
aromatic sulfonate and a fibrous reinforcement (JP-A-6-
299060). The resin compositions disclosed in the foregoing

three documents comprise a phosphate such as
tris(nonylphenyl)phosphate and thus exhibit a low flame
retardance. These resin compositions exhibit a remarkably
reduced heat resistance when a large amount of the foregoing

5   phosphate is incorporated therein in an attempt to enhance
the flame retardance thereof. Further, these documents do
not disclose the fact that the combination of
tris(nonylphenyl)phosphate, bis(nonylphenyl)phenylphosphate
and nonylphenyl diphenylphosphate in predetermined

10   proportions provides remarkable improvements in the balance
of flame retardance, melt flowability, heat resistance,
impact strength and water-resistant gloss retention.

As a further approach for flame-retarding the styrene
resin there has been disclosed a process for the preparation

15   of a triester phosphate comprising a hydrocarbon group
selected from the group consisting of C_{4-22} alkyl group, C_{12-22}
alkenyl group, phenyl group and C_{7-15} alkylphenyl group (alkyl
moiety has from 1 to 9 carbon atoms) (JP-A-3-294284). The
document not only differs from the present invention in that

20   it relates to a preparation process but also neither
discloses nor suggests the fact that the use of a specific
substituent-containing monomeric aromatic phosphate provides
a remarkable improvement in the continuous moldability (non-
volatility) while keeping a styrene resin in particular flame

25   retardant.

A monomeric phosphate comprising a plurality of
isopropyl groups and a flame retardant composition comprising
the same are disclosed (GB2027712 corresponding to US4370281
and JP-B-63-61313) (The term "JP-B" as used herein means an
"examined Japanese patent publication") The total number of
carbon atoms in the substituents in the phosphate of these
documents is as large as from 6 to 47 based on the definition
in the present invention. Further, these documents do not
disclose the fact that only the substituent having a specific
total number of carbon atoms on the number average can give a
sufficient balance between flame retardance and non-
volatility. Moreover, these documents do not refer to the
fact that the incorporation of the specific substituent of
the present invention can provide an enhancement of flame
retardance, particularly dripping flame retardance. Further,
the flame retardant according to these patents comprise a
plurality of isopropyl group as substituents and thus not
only exhibits too high a viscosity to be easily handled but
also exhibits too low a light resistance to be put into
practical use.

Disclosure of the Invention

An object of the present invention is to provide a
flame retardant for styrene resin free from the foregoing
problems, i.e., which causes no mold deposit even after a
prolonged continuous molding (low volatility), and a resin
composition comprising such a flame retardant.

The present inventors have made extensive studies of technique for inhibiting mold deposit as an index of non-volatility. As a result, it has been found that the use of an aromatic phosphate containing a specific substituent as a flame retardant surprisingly provides a drastic enhancement of flame retardance of a styrene resin while inhibiting mold deposit. Thus, the present invention has been worked out.

The present invention relates to, as a main aspect, a low volatility flame retardant for styrene resin comprising an aromatic phosphate represented by formula (I):

(I)

wherein a, b, and c each independently represent an integer of from 1 to 3; and R₁, R₂, and R₃ each independently represent a hydrogen atom or a halogen-free alkyl group having from 1 to 30 carbon atoms, which is not an isopropyl group,

the total number of carbon atoms in the substituents represented by R_1, R_2 and R_3 being from 12 to 25 on an average in one molecule of the aromatic phosphate,

provided that when the flame retardant comprises a
5   plurality of aromatic phosphates having different substituents, the total number of carbon atoms in the substituents R_1, R_2 and R_3 of the flame retardant is represented by a number average in the whole of the flame retardant, which is the sum of the products of the weight
10   fraction of respective aromatic phosphate and the total number of carbon atoms in the substituents in respective aromatic phosphate.

The present invention also relates to a resin composition comprising 100 parts by weight of a styrene resin
15   and from 1 to 50 parts by weight of the flame retardant of the present invention.

Brief Description of Drawings

Fig. 1 illustrates the relationship of the total number of carbon atoms in the substituents of the monomeric
20   aromatic phosphate on the number average with the remaining amount of the monomeric aromatic phosphate after 5 minutes of storage at 250°C determined by thermogravimetric analysis test (TGA method) and the flame retardance (flame-out time: second) of the molded product of resin composition set forth
25   in Table 2;

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Fig. 2 illustrates the results of thermogravimetric analysis test (TGA) of unsubstituted monomeric aromatic phosphate (TPP), alkyl group-substituted monomeric aromatic phosphate (BNPP) and oligomeric aromatic phosphate (fr-1);

Fig. 3 illustrates the average heat release rate of the resin composition comprising the alkyl group-substituted monomeric aromatic phosphate (BNPP) and the oligomeric aromatic phosphate (fr-1) (Example 18 and Comparative Example 25 in Table 4) and the base resin determined by a cone calorimeter;

Fig. 4 illustrates the relationship the content of the oligomeric aromatic phosphate (fr-1) in the resin composition (Table 4) comprising the alkyl group-substituted monomeric aromatic phosphates (BNPP, TNPP) and the origomeric aromatic phosphate (fr-1) and its flame retardance;

Fig. 5 illustrates the relationship of the added parts of PPE based on 100 parts by weight of the rubber-modified styrene resin with MFR, Vicat softening temperature and flame retardance as set forth in Table 10;

Fig. 6 illustrates the relationship of the composition ratio of HIPS as large size particulate rubber to HIPS as small size particulate rubber (of Examples 61 - 65) with dart impact strength (kgcm (2mm thick)), flexural modulus (kg/cm^2) and gloss;

Fig. 7 illustrates the relationship of the composition ratio of GPPS's having different molecular

weights in the rubber-modified styrene resins (of Examples

66 - 68) with dart impact strength (kgcm (2mm thick)) and MFR

(g/10 min.);

Fig. 8 illustrates the relationship of the total

5   number of carbon atoms in the substituents of monomeric

aromatic phosphates obtained by changing the percent

composition of monomeric aromatic phosphates comprising NDPP,

BNPP and TNPP as set forth in Tables 13-1 and 13-2 on the

number average with MFR, Vicat softening temperature,

10   remaining amount after 5 minutes of storage at 250°C (TGA

process) and water-resistant gloss retention;

Fig. 9 illustrates the relationship between the total

content of remaining styrene monomer and dimerization and

trimerization products of styrene in the resin composition

15   set forth in Table 19 and its flame retardance (flame-out

time: second);

Fig. 10 illustrates a typical example of twin-screw

extruder, wherein the shade shows a kneading zone;

Fig. 11 illustrates feed processes for the various

20   components of the resin composition; and

Fig. 12 illustrates the relationship between the

kneadability parameter as an index of kneadability and the

dart impact strength of examples and comparative examples set

forth in Table 26, wherein the ordinate indicates the dart

25   impact strength (kgcm) and the abscissa indicates the

kneadability parameter (extrusion factor/circumferential speed).

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Best Mode for Practicing Invention

The low volatility flame retardant (Component A) for styrene resin of the present invention comprises a monomeric aromatic phosphate having a specific substituent.

It is important that the foregoing monomeric aromatic phosphate be a monomeric type rather than a oligomeric product. Since the monomeric aromatic phosphate is in the form of a monomer, it can efficiently evaporate during the initial stage of combustion. In particular, in the case of a dripping flame retardant styrene resin, the monomeric aromatic phosphate, because of being a monomer, accelerates the plasticity of the styrene resin to enhance the dripping properties thereof during combustion.

The substituents R_1, R_2 and R_3 in the monomeric aromatic phosphate each represent a hydrogen atom or a C_{1-30} alkyl group. It is important that the total number of carbon atoms in the substituents R_1, R_2 and R_3 be from 12 to 25 on the number average as the whole compound. If the number-average total number of carbon atoms falls below 12, an excellent flame retardance can be obtained but a high volatility is given. If the number-average total number of carbon atoms exceeds 25, a reduced flame retardance is given.

The aromatic phosphate satisfying the foregoing requirements exhibits a weight loss of from 0 to 10% by weight at a temperature of 300°C and a weight loss of from 30 to 100% by weight, preferably from 50 to 100% by weight at a

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temperature of 400°C in a heating test in nitrogen
(temperature rising rate: 40°C/min.). In other words, since
the weight loss at 300°C is not more than 10% by weight, no
mold deposit occurs during molding of styrene resin. Thus,

5   the present invention also relates to a low volatility
aromatic phosphate flame retardant, which exhibits a weight
loss of from 0 to 10% by weight at a temperature of 300°C and
from 50 to 100% by weight at a temperature of 400°C, in a
heating test in nitrogen, with a temperature rising rate of

10   40°C/min. Since the aromatic phosphate suddenly evaporate at
a temperature of 400°C during the initial stage of
combustion, the resulting gas phase effect develops flame
retardance. It was further found that since the
incorporation of a specific substituent provides an

15   enhancement of compatibility with styrene resin, the dripping
properties of the resin can be remarkably accelerated. Thus,
the present invention has been worked out.

The monomeric aromatic phosphate constituting the low
volatility flame retardant (Component A) for styrene resin of

20   the present invention is represented by formula (I):

$$\text{(R}_1\text{)}_a\overset{\overset{\displaystyle O}{\parallel}}{-O-P-O-}\text{(R}_3\text{)}_c \qquad \text{(I)}$$

wherein $\underline{a}$, $\underline{b}$, and $\underline{c}$ each independently represent an integer of from 1 to 3; and R_1, R_2, and R_3 each independently represent a hydrogen atom or a halogen-free alkyl group having from 1 to 30 carbon atoms, which is not an isopropyl group,

the total number of carbon atoms in the substituents represented by R_1, R_2 and R_3 being from 12 to 25 on an average in one molecule of the aromatic phosphate,

provided that when the flame retardant comprises a plurality of aromatic phosphates having different substituents, the total number of carbon atoms in the substituents R_1, R_2 and R_3 of the flame retardant is represented by a number average in the whole of the flame retardant, which is the sum of the products of the weight fraction of respective aromatic phosphate and the total number of carbon atoms in the substituents in respective aromatic phosphate.

In the monomeric aromatic phosphate of the present
invention, the total number of carbon atoms in the
substituents R_1, R_2 and R_3 is preferably from 14 to 22, more
preferably from 16 to 20, most preferably from 17 to 19, on
5   the number average.

Specific examples of these substituents include a
nonyl group, a butyl group such as t-butyl, a t-amyl group, a
hexyl group, a cyclohexyl group, a heptyl group, an octyl
group, a decyl group, an undecyl group, a dodecyl group, a
10   tridecyl group, a tetradecyl group, a pentadecyl group, a
hexadecyl group, a heptadecyl group, an octadecyl group, a
nonadecyl group, and an octadodecyl group. One or a
plurality of substituents may substitute for one aromatic
ring on any position of ortho, meta or para, preferably the
15   para position. It is most preferred that the total number of
carbon atoms in the alkyl group which substitutes on one
monomeric phosphate be from 12 to 25. A monomeric phosphate
having a plurality of aromatic rings substituted by one alkyl
group has better heat resistance and water resistance than a
20   monomeric phosphate having only one aromatic ring substituted
by only one long-chain alkyl group. For example, even if the
total number of carbon atoms in the alkyl group as a
substituent is 18, bis(nonylphenyl) phenylphosphate has a
higher heat resistance and is more preferred than
25   octadecylphenyl diphenylphosphate.

Particularly preferred among the flame retardants of the present invention is a monomeric phosphate wherein at least one of R_1, R_2 and R_3 is a nonyl group. The most preferred among the flame retardants of the present invention

5   is bis(nonylphenyl)phenylphosphate wherein R_1 and R_2 each are a nonyl group and R_3 is a hydrogen atom. These monomeric phosphates can exert a great effect particularly when incorporated in the flame retardant in an amount of not less than 50% by weight. Further, these monomeric phosphates

10   exhibit excellent flame dripping properties. The monomeric phosphates are extremely excellent as V-2 rank flame retardant in accordance with the flame retardance standard based on UL-94. This fact has never been known heretofore.

From the standpoint of non-volatility, it is

15   necessary that the total number of carbon atoms in the substituents satisfy the requirements of the present invention. If the content of the compounds wherein the total number of carbon atoms in the substituents falls below 12 is not more than 20% by weight, a higher non-volatility can be

20   exerted.

From the standpoint of thermal stability, particularly thermal discoloration resistance, of the flame retardant, it is preferred that the acid value as defined in JIS-K6751 as an index of remaining acidic substance be not

25   more than 1 mgKOH/g, more preferably not more than 0.5 mgKOH/g, and/or the alkylphenol content be not more than 1%

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by weight, more preferably not more than 0.5% by weight. It

is further preferred that the total content of aluminum,

magnesium, sodium and antimony be not more than 1,000 ppm by

weight. It is also preferred to incorporate a hindered

5   phenol antioxidant in the flame retardant in an amount of

from 1 to 1,000 ppm by weight, since the thermal stability

can be drastically enhanced.

From the standpoint of light resistance, it is

preferred that the substituents R_1, R_2 and R_3 be an alkyl

10   group which is little branched, particularly a linear alkyl

group or an alkyl group having only one branch, rather than

an aryl group. Even if branched at one position, an alkyl

group having not more than 5 carbon atoms exhibits a poor

light resistance. A monomeric phosphate having an isopropyl

15   group exhibits an extremely poor light resistance.

Moreover, the number of substituents on one aromatic

ring in the aromatic phosphate is preferably one. A

monomeric phosphate having a plurality of substituents on one

aromatic ring exhibits a high viscosity. This viscosity

20   rises with the number of substituents on one aromatic ring.

If the viscosity of the monomeric phosphate is raised, the

compound not only suffers a handling problem but also can

hardly be purified, causing the foregoing impurities to be

left and hence deteriorating the light resistance and thermal

25   discoloration resistance thereof.

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The most preferred combination of monomeric aromatic phosphates of the present invention comprises nonylphenyl diphenylphosphate (NPDP, represented by formula (I) where R_1 and R_2 each represent a hydrogen atom and R_3 represents a nonyl group), bis(nonylphenyl) phenylphosphate (BNPP, represented by formula (I) where R_1 represents a hydrogen atom and R_2 and R_3 each represent a nonyl group) and tris(nonylphenyl)phosphate (TNPP, represented by formula (I) where R_1, R_2, and R_3 each represent a nonly group), wherein the total number of the substituents R_1, R_2 and R_3 is from 12 to 25, preferably from 14 to 22, more preferably from 16 to 20, most preferably from 17 to 19 on the number average. In order to satisfy the foregoing number average of the total number of carbon atoms, NPDP content is generally from 1 to 80% by weight, preferably from 1 to 50% by weight, more preferably from 1 to 30% by weight, most preferably from 1 to 10% by weight, BNPP content is generally from 1 to 98% by weight, preferably from 20 to 90% by weight, more preferably from 30 to 80% by weight, most preferably from 40 to 80% by weight, and TNPP content is generally from 1 to 98% by weight, preferably from 1 to 70% by weight, more preferably from 5 to 60% by weight, most preferably from 5 to 50% by weight. The flame retardant having such a combination is excellent particularly in the balance of flame retardance, melt flowability, heat resistance, impact strength, water-resistant gloss retention, and surface hardness of the molded

product thus obtained. The mixing of monomeric aromatic

phosphates having different numbers of substituted nonyl

groups in predetermined amounts can exert a specific effect.

NPDP exerts a high plasticizing effect. NPDP not only acts

5   as a melt flowability improver but also exerts a very high

effect of enhancing flame retardance. TNPP not only exerts a

high effect of providing non-volatility and heat resistance

but also exhibits an extremely excellent water-resistant

gloss retention. BNPP can well balance the foregoing

10   properties. The compounding of the three components in

predetermined amounts can provide well-balanced properties

which cannot be obtained by single use of one of these

components. In particular, the enhancement of water-

resistant gloss retention and surface hardness of molded

15   products cannot be expected from the conventional knowledge.

The preparation of the monomeric aromatic phosphate

of the present invention can be accomplished by a known

method disclosed, e.g., in JP-A-1-95149 and JP-A-3-294284.

Examples of the known method include a method which comprises

20   the reaction of an alkylphenol with phosphorus oxychloride in

the presence of aluminum chloride anhydride as a catalyst

under heating, and a method which comprises the oxidation of

triester phosphite with oxygen to convert it to the

corresponding aromatic phosphate.

25   In the case where the low volatility flame retardant

for styrene resin of the present invention is added to a

styrene resin to prepare a resin composition, it is preferred
that the flame retardant be incorporated in the resin
composition in an amount of from 1 to 50 parts by weight,
more preferably from 1 to 20 parts by weight, most preferably
from 3 to 8 parts by weight, per 100 parts by weight of the
styrene resin.

The styrene resin (Component B) in which the low
volatility flame retardant for styrene resin of the present
invention can be incorporated is a rubber-modified styrene
resin and/or an unmodified styrene resin and is not
specifically limited so far as it can be compatible or
homogeneously dispersed with Component A. Preferably, a
rubber-modified styrene resin or a mixture of a rubber-
modified styrene resin and an unmodified styrene resin is
used. The rubber-modified styrene resin is a polymer
comprising a matrix of vinyl aromatic polymer having a
particulate rubber-like polymer dispersed therein and can be
obtained by the known bulk polymerization, bulk suspension
polymerization, solution polymerization or emulsion
polymerization of a monomer mixture comprising an aromatic
vinyl monomer and optionally a vinyl monomer copolymerizable
therewith in the presence of a rubber-like polymer.

Examples of such a resin include an impact-resistant
polystyrene, an ABS resin (acrylonitrile-butadiene-styrene
copolymer), an AAS resin (acrylonitrile-acryl rubber-styrene

copolymer), and an AES resin (acrylonitrile-ethylenepropylene rubber-styrene copolymer).

The foregoing rubber-like polymer should exhibit a glass transition temperature (Tg) of not higher than -30°C.
5   If the glass transition temperature exceeds -30°C, the resulting composition exhibits a reduced impact resistance.

Examples of such a rubber-like polymer include diene rubber such as (polybutadiene, poly(styrene-butadiene) and poly(acrylonitrile-butadiene)), saturated rubber obtained by
10   hydrogenation of the foregoing diene rubber, isoprene rubber, chloroprene rubber, acrylic rubber (such as poly(butyl acrylate)), and an ethylene-propylene-diene monomer terpolymer (EPDM). Particularly preferred among these rubber-like polymers is diene rubber.

15   Examples of the aromatic vinyl monomer as an essential component to be incorporated in the graft-polymerizable monomer mixture which undergoes polymerization in the presence of the foregoing rubber-like polymer include styrene, α-methylstyrene, and paramethylstyrene. Most
20   preferred among these aromatic vinyl monomers is styrene. Styrene can be copolymerized as a main component with the foregoing other aromatic vinyl monomers.

As the components constituting the rubber-modified styrene resin there may be incorporated one or more monomer
25   components copolymerizable with the aromatic vinyl monomer as necessary. If the oil resistance of the composition needs to

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be enhanced, an unsaturated nitrile monomer such as acrylonitrile and methacrylonitrile may be used.

If it is necessary to reduce the melt viscosity during blending, an acrylate having a C_{1-8} alkyl group may be used. Further, if it is necessary to further enhance the heat resistance of the resin composition, a monomer such as α-methylstyrene, acrylic acid, methacrylic acid, maleic anhydride and N-substituted maleimide may be copolymerized. Among these, α-methylstyrene and butyl acrylate are excellent in providing dripping flame retardance. The content of the vinyl monomer copolymerizable with the foregoing vinyl aromatic monomer in the monomer mixture is generally from 0 to 40% by weight.

The content of the rubber-like polymer in the rubber-modified styrene resin is preferably from 5 to 80% by weight, particularly from 10 to 50% by weight. The content of the graft-copolymerizable monomer mixture in the rubber-modified styrene resin is preferably from 20 to 95% by weight, more preferably from 50 to 90% by weight. Within this range, the resin composition exhibits an improved balance between impact resistance and rigidity. Further, the diameter of the particulate rubber in the styrene polymer is preferably from 0.1 to 5.0 μm, particularly from 0.2 to 3.0 μm, most preferably from 1.0 to 2.0 μm. Within this range, the impact resistance of the rubber-modified styrene resin is enhanced.

The reduced viscosity ηSP/C of the resin moiety as a
measure of the molecular weight of the rubber-modified
styrene resin is preferably from 0.30 to 0.80 dl/g, more
preferably from 0.40 to 0.60 dl/g (as measured with 0.5 g/dl

5   at a temperature of 30°C in a toluene solution if the matrix
resin is a polystyrene or in methyl ethyl ketone if the
matrix resin is an unsaturated nitrile-aromatic vinyl
copolymer). As methods for satisfying the foregoing
requirements for the reduced viscosity ηSP/C of the rubber-

10   modified styrene resin, there may be used the adjustment of
amount of polymerization initiator, polymerization
temperature, amount of chain transfer agent, etc.

In general, a rubber-modified styrene resin having a
reduced viscosity ηSP/C of from 0.40 to 0.60dl/g is excellent

15   in melt flowability and flame retardance, particularly
dripping flame retardance, but exhibits a poor impact
strength. The inventors conducted high degree grafting of a
vinyl aromatic monomer on a conjugated diene polymer the most
of remaining unsaturated bonds of which are 1,4-bonds in the

20   presence of an organic peroxide having a high hydrogen
abstracting capacity. As a result, a rubber-modified styrene
resin exhibiting high impact strength and rigidity having a
specific particle diameter distribution in the dispersed
phase of conjugated diene polymer was successfully prepared.

25   In some detail, a polymerization stock solution which
comprises from 60 to 96% by weight of styrene and optionally

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other vinyl aromatic monomers copolymerizable with styrene, from 4 to 15% by weight of a conjugated diene polymer 95% or more of the remaining unsaturated bonds of which are 1,4-structures or partially hydrogenated conjugated diene polymer, and an organic peroxide having a hydrogen abstracting capacity ε of not less than 35 in an amount of from 0.0002 to 0.0006 equivalents to the foregoing vinyl aromatic monomer such as styrene, is continuously supplied into a multi-stage polymerization apparatus in such a manner that the solution resides in a plug flow type polymerization reactor until the percent conversion of the vinyl aromatic monomer reaches 30% while the polymerization temperature and solution supplying rate are being controlled such that the average polymerization rate until the percent conversion of the vinyl aromatic monomer reaches at least 30% is from 10 to 15%/hr, whereby the desired rubber-modified styrene resin can be prepared. The term "hydrogen abstracting capacity ε" as used herein is meant to indicate the quotient obtained by dividing the number of mols of n-pentadecane dimer produced by heating an about 1 mmol/ℓ n-pentadecane solution of the foregoing organic peroxide to the temperature at which the half-life period is 15 minutes for 150 minutes by the number of mols of the organic peroxide, and then multiplied by 100.

The rubber-modified styrene resin thus obtained comprises small size particles having a diameter of from 0.1 to 0.4μm and large size particles having a diameter of from

1.0 to 8.0μm in the dispersed phase. The proportion of the
small size particles and large size particles in all the
particles are from 10 to 50% and from 50 to 90%,
respectively, as calculated in terms of area. The small size
5   particle comprises a cell structure in a proportion of not
less than 50% as calculated in terms of area. The large size
particle has a structure such that its outermost periphery is
closed and any one of maze, reel and fiber bundle
configurations is incorporated therein, in a proportion of
10   not less than 50% as calculated in terms of area.

The particulate rubber constituting the rubber-
modified styrene resin preferably comprises a small size
particulate rubber having a weight-average particle diameter
of from 0.1 to 0.9 μm and a large size particulate rubber
15   having a weight-average particle diameter of from 1.0 to 3.0
μm from the standpoint of balance of external appearance
(gloss), impact strength and rigidity of the molded product
obtained.

If the weight-average particle diameter of the small
20   size particulate rubber falls below 0.1 μm, the resulting
molded product tends to exhibit a reduced impact strength and
flame retardance. If the weight-average particle diameter of
the small size particulate rubber exceeds 0.9 μm, the
resulting molded product tends to exhibit a reduced rigidity
25   and a deteriorated external appearance (gloss). Further, if
the weight-average particle diameter of the large size

particulate rubber falls below 1.0 μm, the resulting molded product tends to exhibit a reduced impact strength and flame retardance. If the weight-average particle diameter of the large size particulate rubber exceeds 3.0 μm, the resulting molded product tends to exhibit a reduced impact strength and rigidity and a deteriorated external appearance (gloss).

The foregoing small size particulate rubber has a capsule structure made of a block copolymer of styrene and 1,3-butadiene (particle structure having only one occlusion in one rubber particle). The foregoing large size particulate rubber has a "salami" structure or a multidomain structure made of, e.g., polybutadiene (particle structure having a plurality of occlusions in one rubber particle). The proportion of the former in the rubber-modified styrene resin is preferably from 20 to 80% by weight, and the proportion of the latter in the rubber-modified styrene resin is preferably from 20 to 80% by weight.

The foregoing block copolymer of styrene and 1,3-butadiene preferably has a butadiene content of from 15 to 35% by weight. It is a block copolymer structurally represented by SBSB or SBS (in which S represents styrene polymer block and B represents polymer block mainly composed of 1,3-butadiene or butadiene).

The rubber-modified styrene resin comprising large size particulate rubber and small size particulate rubber can be prepared by separately preparing a rubber-modified styrene

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resin containing a small size particulate rubber and a
rubber-modified styrene resin containing a large size
particulate rubber, and then blending these rubber-modified
styrene resins in an extruder, or by mixing the two rubber-

5   modified styrene resins in a polymerization reactor. In some
detail, a bulk polymerization process is preferably employed
which comprises supplying a homogeneous polymerization stock
solution comprising a rubber-like polymer, a monomer mixture
and a polymerization solvent into an agitated continuous

10   multi-stage bulk polymerization reactor where it is
continuously subjected to polymerization and devolatilization
In the case of preparation by bulk polymerization process,
the particle diameter of the particulate rubber is controlled
by the number of revolutions for agitation. The more the

15   number of revolutions is, the smaller is the particle
diameter. The less the number of revolutions is, the larger
is the particle diameter.

        The low volatility flame retardant for styrene resin
of the present invention can be incorporated in a resin

20   composition comprising a styrene resin blended with other
thermoplastic resins. For example, a polyphenylene ether
resin, a polyamide resin, a polyester resin, a polyphenylene
sulfide resin, a polycarbonate resin or a polymethacrylate
resin may be used singly, and two or more of these resins may

25   be used in admixture. Preferred examples of the
thermoplastic resin which can be incorporated in the styrene

resin include a polyphenylene ether thermoplastic resin and a
polycarbonate thermoplastic resin. The content of the other
thermoplastic resin in the mixture of the styrene resin and
the other thermoplastic resin is preferably from 0 to 90% by
5   weight, more preferably from 0 to 70% by weight, most
preferably from 3 to 40% by weignt.

The polyphenylene ether (Component C) which can be
incorporated in the styrene resin is a homopolymer and/or
copolymer comprising a repeating unit represented by formula
10   (II):

$$\left(\!\!\! \begin{array}{c} R^3 \qquad R^2 \\ \underline{} \underset{R^4 \qquad R^1}{\bigcirc}\!\!-O\underline{} \end{array} \!\!\!\right) \qquad\qquad (II)$$
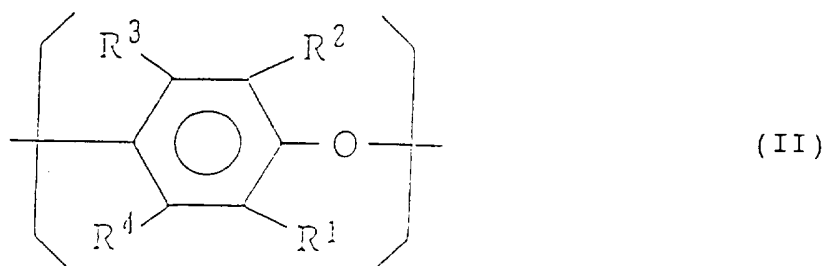
wherein R^1, R^2, R^3 and R^4 each are selected from the group
consisting of a hydrogen atom, a hydrocarbon group and a
substituted hydrocarbon group, and may be the same or
15   different.

Specific preferred examples of the polyphenylene
ether include poly(2,6-dimethyl-1,4-phenyleneether), and
copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol.
Particularly preferred among these polyphenylene ethers is
20   poly(2,6-dimethyl-1,4-phenyleneether). The process for the
preparation of such a polyphenylene ether is not specifically

limited. For example, 2,6-xylenol can be subjected to
oxidative polymerization in the presence of a complex of
cuprous salt with amine as a catalyst as described in U.S.
Patent 3,306,874 to easily prepare such a polyphenylene

5   ether. Besides this process, processes as described in U.S.
Patents 3,306,875, 3,257,357, and 3,257,358, JP-B-52-17880,
and JP-A-50-51197 can be employed to easily prepare such a
polyphenylene ether.

The reduced viscosity ηSP/C of the foregoing

10   polyphenylene ether to be used in the present invention is
preferably from 0.20 to 0.70 dl/g, more preferably from 0.30
to 0.60 dl/g (as measured with 0.5 g/dl in a chloroform
solution at a temperature of 30°C) from the standpoint of
melt flowability and flame retardance, particularly dripping

15   flame retardance. Examples of methods for satisfying the
foregoing requirements for the reduced viscosity ηSP/C of the
polyphenylene ether include control of the amount of the
catalyst to be used in the preparation of the polyphenylene
ether.

20   The amount of the polyphenylene ether to be used is
preferably from 1 to 40 parts by weight, more preferably from
1 to 10 parts by weight, most preferably from 3 to 8 parts by
weight, per 100 parts by weight of the styrene resin used.

The aromatic polycarbonate as the thermoplastic resin

25   which can be incorporated in the styrene resin can be
obtained by a phosgene process in which phosgene is bubbled

into an aromatic divalent phenol compound in the presence of a caustic alkali and a solvent or by an ester interchange process in which an aromatic divalent phenol compound and diethyl carbonate are subjected to ester interchange in the presence of a catalyst. The preferred viscosity-average molecular weight of the aromatic homopolycarbonate or copolycarbonate thus obtained is from 10,000 to 100,000.

Examples of the foregoing divalent phenol compound include 2,2'-bis(4-hydroxyphenyl)propane, 2,2'-bis(4-hydroxy-3,5-dimethylphenyl)propane, bis(4-hydroxyphenyl)methane, 1,1'-bis(4-hydroxyphenyl)ethane, 2,2'-bis(4-hydroxyphenyl)butane, 2,2'-bis(4-hydroxy-3,5-diphenyl)butane, 2,2'-bis(4-hydroxy-3,5-dipropylphenyl)propane, 1,1'-bis(4-hydroxyphenyl) cyclohexane, and 1-phenyl-1,1'-bis(4-hydroxyphenyl)ethane. Particularly preferred among these divalent phenol compounds is 2,2'-bis(4-hydroxyphenyl) propane (bisphenol A). The divalent phenol compounds of the present invention may be used singly or in combination.

The amount of the polycarbonate to be used is preferably from 1 to 40 parts by weight, more preferably from 1 to 10 parts by weight, most preferably from 3 to 7 parts by weight, per 100 parts by weight of the styrene resin used.

The low volatility flame retardant for styrene resin of the present invention may be used with a polyorganopolysiloxane (Component D) as necessary depending on the kind of the resin composition to relax the orientation

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of the styrene resin. If a high shearing force is used during molding, the resulting molded product has orientation left therein, inhibiting the dripping on burning. Thus, the incorporation of a polyorganopolysiloxane having a specific kinematic viscosity renders the molecular chain slippery, relaxing the orientation of the resin composition. As a result, the dripping properties of the molded product of resin composition can be improved. The kinematic viscosity (25°C) of the foregoing polyorganosiloxane is preferably from 30 to 20,000 CS, more preferably from 40 to 1,000 CS, most preferably from 50 to 100 CS. If the kinematic viscosity of the foregoing polyorganosiloxane falls below 30 CS, the polyorganosiloxane exhibits a high volatility and thus causes mold stain. If the kinematic viscosity of the foregoing polyorganosiloxane exceeds 20,000 CS, the resulting effect of relaxing the orientation of the styrene resin is reduced.

As the polyorganosiloxane as Component D, a polydimethylsiloxane, i.e., so-called silicone oil, is preferably used.

The amount of the polyorganosiloxane to be used is preferably from 0.01 to 10 parts by weight, more preferably from 0.1 to 5 parts by weight, most preferably from 0.3 to 3 parts by weight, per 100 parts by weight of the styrene resin used.

The low volatility flame retardant for styrene resin of the present invention may be used with a flame retardant

(Component E) other than the flame retardant of the present invention (Component A), such as an organic phosphorus compound, red phosphorus, an inorganic phosphorus salt, an inorganic flame retardant or the like, as necessary depending

5   on the kind of the resin composition.

The amount of Component E to be used is preferably from 1 to 40 parts by weight, more preferably from 1 to 20 parts by weight, most preferably from 5 to 10 parts by weight, per 100 parts by weight of the styrene resin used.

10   Examples of the organic phosphorus compound as Component E include phosphine, phosphine oxide, biphosphine, phosphonium salt, phosphinate, phosphate, and phosphite. Specific examples of these organic phosphorus compounds include methyl neopentyl phosphite, pentaerythritol diethyl

15   diphosphite, methyl neopentyl phosphonate, phenyl neopentyl phosphate, pentaerythritol diphenyl diphosphate, dicyclopentyl hypodisphosphate, dineopentyl hypophosphite, phenylpyrocatechol phosphite, ethylpyrocatechol phosphate, and dipyrocatechol hypodiphosphate.

20   An oligomeric aromatic phosphate such as tetraphenyl bisphenol A polyphosphate may be blended in the resin composition to an extent such that the flame retardance thereof cannot be affected.

Examples of the red phosphorus which can be used as

25   Component E include ordinary red phosphorus. Other examples of the red phosphorus include red phosphorus coated with a

film of metal hydroxide selected from the group consisting of
aluminum hydroxide, magnesium hydroxide, zinc hydroxide and
titanium hydroxide; red phosphorus coated with a film made of
metal hydroxide selected from the group consisting of
aluminum hydroxide, magnesium hydroxide, zinc hydroxide and
titanium hydroxide and a thermoplastic resin; and red
phosphorus coated sequentially with a film of metal hydroxide
selected from the group consisting of aluminum hydroxide,
magnesium hydroxide, zinc hydroxide and titanium hydroxide
and with a film of thermoplastic resin on the film of metal
hydroxide.

A representative example of the inorganic phosphorus
salt which can be used as Component E include ammonium
polyphosphate.

Examples of the inorganic flame retardant which can
be used as Component E include hydrate of inorganic metal
compound such as hydrate of aluminum hydroxide, magnesium
hydroxide, dolomite, hydrotalcite, calcium hydroxide, barium
hydroxide, basic magnesium carbonate, zirconium hydroxide and
tin hydroxide, zinc borate, zinc metaborate, barium
metaborate, zinc carbonate, magnesium carbonate, calcium
carbonate, and barium carbonate. These inorganic flame
retardants may be used singly or in combination.
Particularly preferred among these inorganic flame retardants
are those selected from the group consisting of magnesium
hydroxide, aluminum hydroxide, basic magnesium carbonate and

hydrotalcite, which can exert a good flame retarding effect and are economically advantageous.

The low volatility flame retardant for styrene resin of the present invention may be used with one or more auxiliary flame retardants (Component F) selected from the group consisting of a triazine skeleton-containing compound, a novolak resin, a metal-containing compound, a silicone resin, a vinyl group-containing silicone oil, silica, aramide fibers, a fluorine resin and polyacrylonitrile fibers as necessary depending on the kind of the resin composition.

The amount of Component F to be used is preferably from 0.001 to 40 parts by weight, more preferably from 1 to 20 parts by weight, most preferably from 5 to 10 parts by weight, per 100 parts by weight of the styrene resin used.

The triazine skeleton-containing compound which can be used as Component F is a component for enhancing the flame retardance as an aid for the phosphorus flame retardant. Specific examples of the triazine skeleton-containing compound include melamine, melam, melem, mellon (product of three molecule deammonization of three melem molecules at a temperature of not lower than 600°C), malamine cyanurate, melamine phosphate, succinoguanamine, adipoguanamine, methylglutaloguanamine, melamine resin, and BT resin. Particularly preferred among these triazine skeleton-containing compounds is melamine cyanurate from the standpoint of non-volatility. The structural formulae of

melam, melem, mellon, melamine cyanurate, melamine phosphate,

succinoguanamine, melamine resin, and BT resin are shown

below.

melam

5
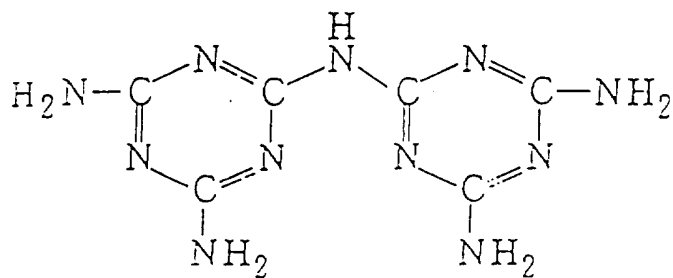
melem
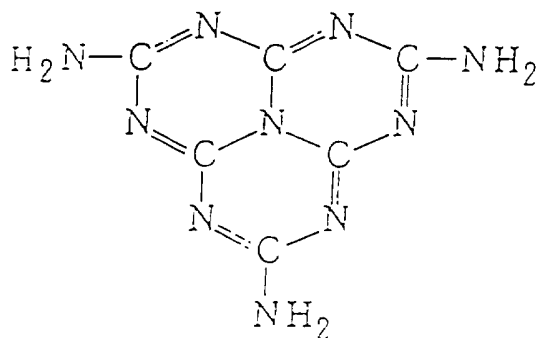
melamine cyanurate

<u>melamine phosphate</u>

$$H_2N-C \underset{N}{\overset{N}{=}} C-NH_3^+ \cdot H_2PO_4^-$$

$$NH_2$$

<u>succinoquanamine</u>

$$H_2N-C \quad C-CH_2CH_2-C \quad C-NH_2$$

$$NH_2 \qquad NH_2$$

5   <u>melamine resin</u>

$$-HN-C \quad C-NH-CH_2-HN-C \quad C-NH\sim$$

$$NH \qquad NH$$

<u>BT resin</u>

$$-Ar_1-O-C \quad C-O-Ar_1-O-C \qquad C-O-Ar_1-$$

$$O-Ar_1$$

$$Ar_1: \quad -C_6H_4-C(CH_3)_2-C_6H_4- \qquad Ar_2: \quad -C_6H_4-CH_2-C_6H_4-$$
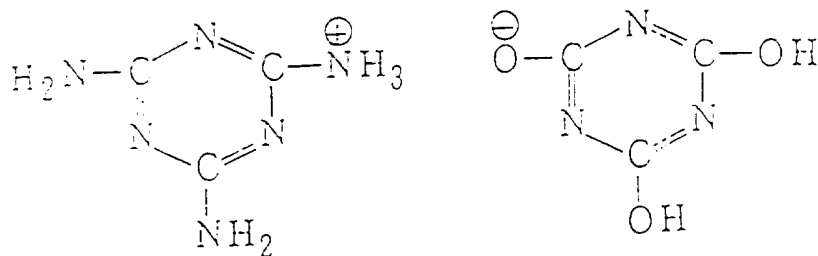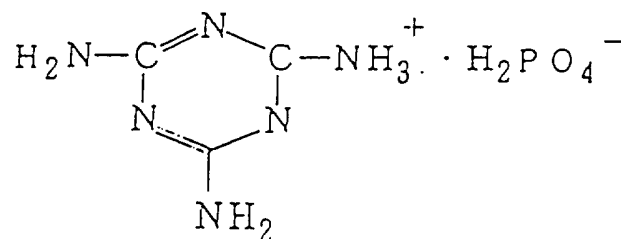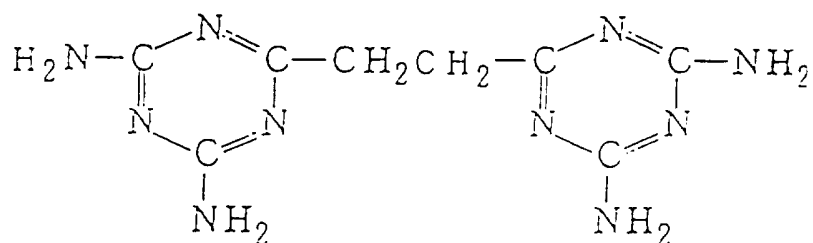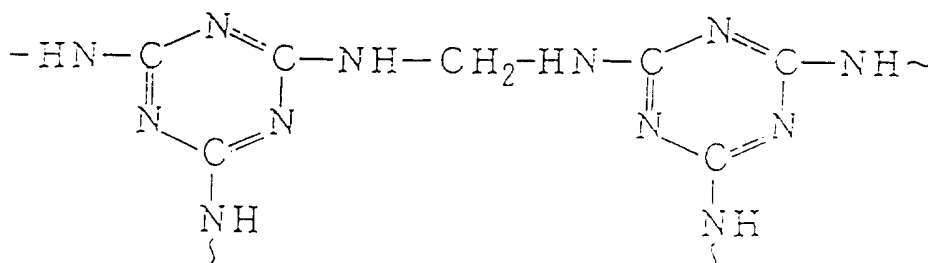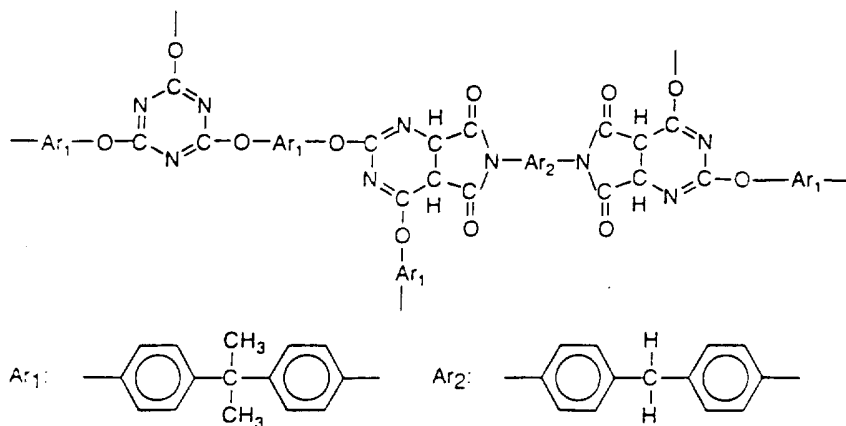
The novolak resin as Component F is an auxiliary

flame retardant. It also serves as a melt flowability and

heat resistance improver when used in combination with a

hydroxyl group-containing aromatic phosphate. This resin is

5   a thermoplastic resin obtained by the condensation of a

phenol and an aldehyde in the presence of an acid catalyst

such as sulfuric acid and hydrochloric acid. Its preparation

process is described, e.g., in "High Molecular Experiment 5

(Polycondensation and Polyaddition)", pp. 437 - 455, Kyoritsu

10   Shuppan.

An example of the process for the preparation of a

novolak resin is shown below.

monomethylolphenol
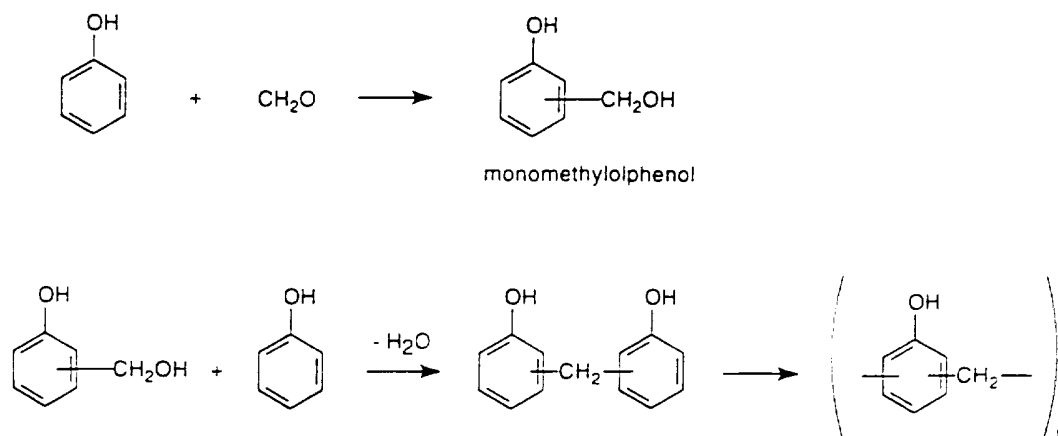
Examples of the foregoing phenols include phenol, o-

15   cresol, m-cresol, p-cresol, 2,5-dimethylphenol, 3,5-

dimethylphenol, 2,3,5-trimethylphenol, 3,4,5-trimethylphenol,

p-t-butylphenol, p-n-octylphenol, p-stearylphenol, p-

phenylphenol, p-(2-phenylethyl)phenol, o-isopropylphenol, o-

isopropylphenol, m-isopropylphenol, p-methoxyphenol, p-

phenoxyphenol, pyrocatechol, resoricinol, hydroquinone, salicylaldehyde, salicylic acid, p-hydroxybenzoic acid, methyl p-hydroxybenzoate, p-cyanophenol, o-cyanophenol, p-hydroxybenzenesulfonic acid, p-hydroxybenzenesulfonamide, cyclohexyl p-hydroxybenzenesulfonate, 4-hydroxyphenylphenylphosphinic acid, methyl 4-hydroxyphenylphenylphosphinate, 4-hydroxyphenylphosphonic acid, ethyl 4-hydroxyphenylphosphonate, and diphenyl 4-hydroxyphenylphosphonate.

Examples of the foregoing aldehydes include formaldehyde, acetaldehyde, n-propanal, n-butanal, isopropanal, isobutylaldehyde, 3-methyl-n-butanal, benzaldehyde, p-tollylaldehyde, and 2-phenylacetaldehyde.

The metal-containing compound which can be used as Component F is a metal oxide and/or metal powder. Examples of the metal oxide include aluminum oxide, iron oxide, titanium oxide, manganese oxide, magnesium oxide, zirconium oxide, zinc oxide, molybdenum oxide, cobalt oxide, bismuth oxide, chromium oxide, tin oxide, antimony oxide, nickel oxide, copper oxide, tungsten oxide, etc., singly or in composite of two or more of them. Examples of the metal powder include aluminum, iron, titanium, manganese, zinc, molybdenum, cobalt, bismuth, chromium, nickel, copper, tungsten, tin, antimony, etc., singly or in composite of two or more of them (alloy).

The silicone resin which can be used as Component F is a silicone resin having a three-dimensional network composed of SiO_2, $RSiO_{3/2}$, R_2SiO and $R_3SiO_{1/2}$ as structural units wherein R represents an alkyl group such as methyl, ethyl and propyl, an aromatic group such as phenyl and benzyl, or a substituent comprising the above alkyl or aromatic group having a vinyl group incorporated therein. In particular, a vinyl group-containing silicone resin is preferred. Such a silicone resin can be obtained by the co-hydrolysis of an organohalosilane corresponding to the foregoing structural unit.

The vinyl group-containing silicone oil which can be used as Component F is a polydiorganosiloxane made of a chemical bond unit represented by the following formula:

$$-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}}O-$$

wherein R represents one or more kinds of substituents selected from the group consisting of a C_{1-8} alkyl group, a C_{6-13} aryl group and a vinyl-containing groups represented by the following formulae. Particularly preferred among these substituents is one containing vinyl group in its molecule.

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$$-C_3H_6-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

$$CH_2=CH-$$
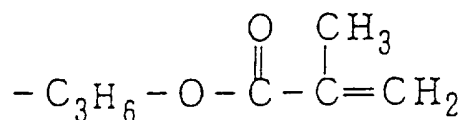
The kinematic viscosity of the foregoing vinyl group-containing silicone oil is preferably from 600 to 1,000,000 CP (25°C), more preferably from 90,000 to 150,000 CP (25°C).

The silica which can be used as Component F is an amorphous silicon dioxide, preferably a hydrocarbon compound-coated silica obtained by treating the surface of silica with a silane coupling agent made of hydrocarbon compound, more preferably a vinyl group-containing hydrocarbon compound-coated silica.

Examples of the foregoing silane coupling agent include vinyl group-containing silane such as p-styryl trimethoxysilane, vinyl trichlorosilane, vinyl tris(β-methoxyethoxy)silane, vinyl triethoxysilane, vinyl trimethoxysilane and γ-methacryloxypropyl trimethoxysilane; epoxysilane such as β-(3,4-epoxycyclohexyl)ethyl trimethoxysilane, γ-glycidoxypropyl trimethoxysilane and γ-

glycidoxypropyl triethoxysilane; and aminosilane such as N-
β(aminoethyl)γ-aminopropyl trimethoxysilane, N-
β(aminoethyl)γ-aminopropylmethyldimethoxysilane, γ-
aminopropyl triethoxysilane and N-phenyl-γ-aminopropyl

5   trimethoxysilane. Particularly preferred among these silane
coupling agents is a silane coupling agent having a unit
structurally akin to the thermoplastic resin. For example,
p-styryl trimethoxysilane is preferred for a styrene resin.

The treatment of the surface of silica with a silane

10   coupling agent can be roughly divided into two groups, i.e.,
a wet process and a dry process. The wet process comprises
treating silica in a silane coupling agent solution, and then
drying. The dry process comprises charging silica in an
apparatus capable of agitating at a high speed such as

15   Henschel mixer, slowly adding dropwise a silane coupling
agent solution to the material with stirring, and then heat-
treating.

The aramide fiber which can be used as Component F
preferably has an average diameter of from 1 to 500 μm and an

20   average fiber length of from 0.1 to 10 mm. It can be
prepared by dissolving isophthalamide or polyparaphenylene
terephthalamide in an amide polar solvent or sulfuric acid,
and then solution-spinning the material in a wet or dry
process.

25   The fluorine resin which can be used as Component F
is a resin comprising fluorine atoms incorporated therein.

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Specific examples of such a fluorine resin such as polymonofluoroethylene, polydifluoroethylene, polytrifluoroethylene, polytetrafluoroethylene, and tetrafluoroethylene/hexafluoropropylene copolymer. Further, such a fluorine resin may be used in combination with a monomer copolymerizable with the foregoing fluorine-containing monomer.

The polyacrylonitrile fiber which can be used as Component F preferably has an average diameter of from 1 to 500 μm and an average fiber length of from 0.1 to 10 mm. The polyacrylonitrile fiber can be prepared by a dry spinning process which comprises dissolving a polymer in a solvent such as dimethylformamide, and then dry-spinning the material in a flow of 400°C air or by a wet spinning process which comprises dissolving a polymer in a solvent such as nitric acid, and then wet-spinning the material in water.

The low volatility flame retardant for styrene resin of the present invention may be used with one or more melt flowability improver (Component G) selected from the group consisting of a copolymer resin made of aromatic vinyl unit and acrylic ester unit, an aliphatic hydrocarbon, a higher aliphatic acid, a higher aliphatic ester, a higher aliphatic amide, a higher aliphatic alcohol and a metallic soap as necessary depending on the kind of the resin composition.

The amount of Component G to be used is preferably from 0.1 to 20 parts by weight, more preferably from 0.5 to

10 parts by weight, most preferably from 1 to 5 parts by
weight, per 100 parts by weight of the rubber-modified
styrene resin used.

Examples of the aromatic vinyl unit constituting the
copolymer resin as Component G include styrene, α-
methylstyrene, paramethylstyrene, p-chlorostyrene, p-
bromostyrene, and 2,4,5-tribromostyrene. Most preferred
among these aromatic vinyl units is styrene. Alternatively,
styrene as a main component and the foregoing other aromatic
vinyl monomers may be subjected to copolymerization. The
foregoing acrylic ester unit include an acrylic ester made of
a C_{1-8} alkyl group such as methyl acrylate and butyl acrylate.
The content of the acrylic ester unit in the copolymer resin
is preferably from 3 to 40% by weight, more preferably from 5
to 20% by weight. The solution viscosity as an index of the
molecular weight of the foregoing copolymer resin is
preferably from 2 to 10 cP (centipoise) (as measured with a
10 wt% MEK solution at a temperature of 25°C). If the
solution viscosity of the copolymer resin falls below 2 cP,
the resulting impact strength is reduced. If the solution
viscosity of the copolymer resin exceeds 10 cP, the resulting
effect of enhancing melt flowability is reduced.

Examples of the aliphatic hydrocarbon working aid as
Component G include liquid paraffin, natural paraffin,
microwax, polyolefin wax, synthetic wax, partial oxidation
product thereof, fluoride thereof, and chloride thereof.

Examples of the higher aliphatic acid as Component G include a saturated aliphatic acid such as caproic acid, hexadecanoic acid, palmitic acid, stearic acid, phenylstearic acid and ferronic acid; and an unsaturated aliphatic acid such as ricinoleic acid, ricinobelaidic acid and 9-oxy-12-octadecenic acid.

Examples of the higher aliphatic ester as Component G include a monovalent alcohol ester of an aliphatic acid such as methyl phenylstearate and butyl phenylstearate; and a monovalent alcohol ester of a polybasic acid such phthalic diester of phthalic diphenylstearyl. Further examples of such a higher aliphatic ester include a sorbitan ester such as sorbitan monolaurate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate, sorbitan trioleate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate and polyoxyethylene sorbitan monooleate; an aliphatic ester of glycerin monomer such as monoglyceride stearate, monoglyceride oleate, monoglyceride caprinate and monoglyceride behenate; an aliphatic ester of polyglycerin such as polyglycerinstearate, polyglycerinoleate and polyglycerinlaurate; an aliphatic ester having a polyalkylene ether unit such as polyoxyethylene monolaurate, polyoxyethylene monostearate and polyoxyethylene monooleate; and a neopentylpolyolaliphatic ester such as neopentylpolyoldistearic ester.

Examples of the higher aliphatic amide as Component G
include a monoamide of a saturated aliphatic acid such as
amide phenylstearate, amide methylolstearate and amide
methylolbehenate; and an N,N'-2-substituted monoamide such as
diethanolamide.of coconut oil fatty acid and diethanolamide
of oleic acid. Specific examples of such a higher aliphatic
amide include a saturated aliphatic bisamide such as
methylenebis(12-hydroxyphenyl)stearic amide,
ethylenebisstearic amide, ethylenebis(12-
hydroxyphenyl)stearoc amide and hexamethylenebis(12-
hydroxyphenyl)stearic amide , and aromatic bisamide such as
m-xylylenebis(12-hydroxyphenyl)stearic amide.

Examples of the higher aliphatic alcohol as Component
G include a monovalent alcohol such as stearyl alcohol and
cetyl alcohol; a polyvalent alcohol such as sorbitol and
mannitol; polyoxyethylene dodecylamine; and polyoxyethylene
octadecylamine. Specific examples of such a higher aliphatic
alcohol include an allylated ether having polyalkylene ether
unit such as polyoxyethyleneallylated ether; a
polyoxyethylene alkyl ether such as polyoxyethylene lauryl
ether, polyoxyethylene tridodecyl ether, polyoxyethylene
cetyl ether, polyoxyethylene stearyl ether and
polyoxyethylene oleyl ether; a polyoxyethylene alkyl phenyl
ether such as polyoxyethylne octyl phenyl ether and
polyoxyethylene nonyl phenyl ether; and a divalent alcohol
having polyalkylene ether unit such as polyepichlorohydrin

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ether, polyoxyethylene bisphenol A ether, polyoxyethylene ethylene glycol, polyoxypropylene bisphenol A ether and polyoxyethylene polyoxypropylene glycol ether.

The metallic soap as Component G include a salt of the foregoing higher aliphatic acid such as stearic acid with a metal such as barium, calcium, zinc, aluminum and magnesium.

The low volatility flame retardant for styrene resin of the present invention may be used with a thermoplastic elastomer (Component H) as necessary depending on the kind of the resin composition. Examples of such a thermoplastic elastomer include polystyrene, polyolefin, polyester, polyurethane, 1,2-polybutadiene and polyvinyl chloride thermoplastic elastomers. Particularly preferred among these thermoplastic elastomers is polystyrene thermoplastic elastomer.

The amount of Component H to be used is preferably from 0.5 to 20 parts by weight, more preferably from 1 to 10 parts by weight, most preferably from 2 to 5 parts by weight, per 100 parts by weight of the rubber-modified styrene resin used.

The foregoing polystyrene thermoplastic elastomer is a block copolymer of an aromatic vinyl unit and a conjugated diene unit or a block copolymer wherein the foregoing conjugated diene unit is partially hydrogenated.

Examples of the aromatic vinyl monomer constituting the foregoing block copolymer include styrene, α-methylstyrene, paramethylstyrene, p-chlorostyrene, p-bromostyrene, and 2,4,5-tribromostyrene. Most preferred

5   among these aromatic vinyl monomers is styrene. Styrene as a main component and the foregoing other aromatic vinyl monomers may be subjected to copolymerization.

Examples of the conjugated diene monomer constituting the foregoing block copolymer include 1,3-butanediene and

10   isoprene.

The block structure of the block copolymer is preferably a linear block copolymer represented by SB, $S(BS)_n$ (in which n represents an integer of from 1 to 3) or $S(BSB)_n$ (in which n represents an integer of 1 or 2) or a star block

15   copolymer having B moiety as a bond center represented by $(SB)_nX$ (in which n represents an integer of from 3 to 6, and X represents a coupling agent residue such as silicon tetrachloride, tin tetrachloride and a polyepoxy compound) wherein the polymer block composed of aromatic vinyl unit is

20   represented by S and the polymer block composed of conjugated diene and/or partially hydrogenated conjugated diene unit is represented by B. Particularly preferred among these block structures are SB, SBS and SBSB linear block copolymers.

The low volatility flame retardant for styrene resin

25   of the present invention may be used with one or more light resistance improvers (Component I) selected from the group

consisting of ultraviolet light absorber, hindered amine
light stabilizer, antioxidant, halogen-capturing agent,
sunproofing agent, metal inactivating agent and light
quenching agent as necessary depending on the kind of the
5   resin composition if it is required to have light resistance.

The amount of Component I to be used is preferably
from 0.05 to 20 parts by weight, more preferably from 0.1 to
10 parts by weight, most preferably from 1 to 5 parts by
weight, per 100 parts by weight of the styrene resin used.
10   The ultraviolet light absorber as Component I is a
component which absorbs light energy to undergo
intramolecular protonic migration to become a keto type
molecule (benzophenone, benzotriazole) or undergo cis-trans
isomerization (cyano acrylate) to release it as a heat energy
15   and hence protect the resin composition. Examples thereof
inlcude a 2-hydroxybenzophenones such as 2,4-
dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-
hydroxy-4-octoxybenzophenone and 5,5'-methylenebis(2-hydroxy-
4-methoxyenzophenone, a 2-(2'-hydroxyphenyl)benzotriazoles
20   such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-
hydroxy-5'-t-octylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-
di-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-t-
butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-t-5'-
methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-
25   dicumylphenyl)benzotriazole, and 2,2'-methylenebis(4-t-octyl-
6-benzotriazole)phenol, phenyl salicylate, benzoates such as

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resorcinol monobenzoate, 2,4-di-t-butylphenyl-3',5'-di-t-
butyl-4'-hydroxybenzoate and hexadecyl-3,5-di-t-butyl-4-
hydroxybenzoate, substituted oxanilides such as 2-ethyl-2'-
ethoxyoxanilide and 2-ethoxy-4'-dodecyloxanilide, and cyano

5   acrylates such as ethyl-α-cyano-β,β-diphenylacrylate and
methyl-2-cyano-3-methyl-3-(p-methoxyphenyl)acrylate.

The hindered amine light stabilizer as Component I is
a component which decomposes a hydroperoxide produced by
light energy to produce a stable N-O· radical or N-OR or N-OH

10   and hence stabilize the resin composition. Specific examples
of the hindered amine light stabilizer include 2,2,6,6-
tetramethyl-4-piperidylstearate, 1,2,2,6,6-pentamethyl-4-
piperidylstearate, 2,2,6,6-tetramethyl-4-piperidylbenzoate,
bis(2,2,6,6-tetramethyl-4-piperidylsebacate, bis(1,2,3,6,6-

15   pentamethyl-4-piperidyl)sebacate, tetrakis(2,2,6,6-
tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate,
tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)-1,2,3,4-
butanetetracarboxylate, bis(1,2,2,6,6-pentamethyl-4-
piperidyl)di(tridecyl)-1,2,3,4-butanetetracarboxylate,

20   bis(1,2,2,6,6-pentamethyl-4-piperidyl)-2-butyl-2-(3',5'-di-t-
butyl-4-hydroxybenzyl)malonate, 1-(2-hydroxyethyl)-2,2,6,6-
tetramethyl-4-piperidinool/diethyl succinate polycondensate,
1,6-bis(2,2,6,6-tetramethyl-4-piperidylamino)hexane/
dibromoethane polycondensate, 1,6-bis(2,2,6,6-tetramethyl-4-

25   piperidylamino)hexane/2,4-dichloro-6-t-octylamino-s-triazine

polycondensate, 1,6-bis(2,2,6,6-tetramethyl-4-piperidylamino)
hexane/2,4-dichloro-6-morpholino-s-triazine polycondensate.

The antioxidant as Component I is a component which
stabilizes a peroxide radical such as hydroperoxide radical
produced during heat molding or exposure to light or
decomposes a peroxide such as hydroperoxide produced.
Examples of such an oxidation inhibitor include hindered
phenol oxidation inhibitor and peroxide decomposer. The
former acts as a radical chain terminator to inhibit
spontaneous oxidation, and the latter decomposes a peroxide
produced in the system to an alcohol which is more stable to
inhibit spontaneous oxidation.

Specific examples of the hindered phenol antioxidant
as an antioxidant include 2,6-di-t-butyl-4-methylphenol,
styrenated phenol, n-octadecyl-3-(3,5-di-t-butyl-4-
hydroxyphenyl)propionate, 2,2'-methylenebis(4-methyl-6-
butylphenol), 2-t-butyl-6-(3-t-butyl-2-hydroxy-5-
methylbenzyl)-4-methylphenylacrylate, 2-(1-(2-hydroxy-3,5-di-
t-pentylphenyl)ethyl)-4,6-di-t-pentylphenylacrylate, 4,4'-
butylidenebis(3-methyl-6-t-butylphenol), 4,4'-thiobis(3-
methyl-6-t-butylphenol), alkylated bisphenol, tetrakis
(methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)
methane, 3,9-bis(2-(3-(3-t-butyl-4-hydroxy-5-methylphenyl)-
propionyloxy)-1,1-dimethylethyl)-2,4,8,10-tetraoxyspiro(5·5)
undecane.

Specific examples of the peroxide decomposer as an antioxidant include organic phosphorus peroxide decomposers such as trisnonyl phenyl phosphite, triphenyl phosphite and tris(2,4-di-t-butylphenyl)phosphite, and organic sulfur

5   peroxide decomposers such as dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate, pentaerythrityltetrakis(3-laurylthiopropionate), ditridecyl-3,3'-thiodipropionate and 2-mercaptobenzimidazole.

10   The halogen-capturing agent as Component I is a component for catching free halogen produced during heat molding or exposure to light. Specific examples of such a halogen-capturing agent include basic metal salts such as calcium stearate and zinc stearate, hydrotalcite, zeolite,

15   magnesium oxide, organic tin compound, and organic epoxy compounds.

Examples of hydrotalcite as halogen-capturing agent include hydrous or anhydrous basic carbonate of magnesium, calcium, zinc, aluminum, bismuth. These hydrotalcites may be

20   natural or synthetic. Examples of natural hydrotalcites include one represented by the structural formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Examples of synthetic hydrotalcites include $Mg_{0.7}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot 0.54H_2O$, $Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5H_2O$, $Mg_{4.2}Al_2(OH)_{12.4}CO_3$, $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, $Ca_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, and

25   $Mg_{14}Bi_2(OH)_{29.6} \cdot 4.2H_2O$.

Examples of the foregoing zeolite include A type zeolite represented by $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot H_2O$, and zeolite substituted by metals including at least one metal selected from the group consisting of the group II and IV metals.

5   Examples of the substituent metal include Mg, Ca, Zn, Sr, Ba, Zr, and Sn. Particularly preferred among these substituent metals are Ca, Zn, and Ba.

Examples of the foregoing epoxy compound as halogen-capturing agent include epoxidized soybean oil,

10   tris(epoxypropyl)isocyanurate, hydroquinone diglycidyl ether, diglycidyl ester terephthalate, 4,4'-sulfobisphenol·polyglycidyl ether, N-glycidyl phthalimide, hydrogenated bisphenol A glycidyl ether, and alicyclic epoxy compounds such as 3,4-epoxycyclohexylmethyl-3,4-

15   epoxycyclohexanecarboxylate, 2-(3,4-epoxycyclohexylspiro[5,5]-3,4-epoxy)cyclohexane-m-dioxane, bis(3,4-epoxycylohexylmethyl)adipate, vinylcyclohexene dioxide, 4-vinylepoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, 3,4-epoxy-6-methylcyclohexyl-

20   3,4-epoxy-6-methylcyclohexanecarboxylate, methylenebis(3,4-epoxycyclohexane), dicyclopentadiene epoxide, di(3,4-epoxycyclohexylmethyl)ether of ethylene glycol, ethylenebis(3,4-epoxycyclohexanecarboxylate), dioctyl epoxyhexahydrophthalate and di-2-ethylhexyl

25   epoxyhexahydrophthalate.

The sunproofing agent as Component I is a component
for preventing light from reaching the interior of the high
molecular weight compound. Specific examples of the
sunproofing agent include rutile titanium oxide (TiO_2), zinc
oxide (ZnO), chromium oxide (Cr_2O_3), and cerium oxide (CeO_2).

The metal inactivating agent as Component I is a
component which forms a chelate compound by which heavy metal
ions in the resin are inactivated. Specific examples of the
metal inactivating agent include acid amine derivative,
benzotriazole, and derivative thereof.

The light quenching agent as Component I is a
component for inactivating a functional group such as
hydroperoxide and carbonyl group optically excited in the
high molecular compound by transferring energy. As such a
light quenching agent there is known an organic nickel.

One of preferred combinations constituting the low
volatility flame retardant for styrene resin of the present
invention comprises a flame retardant selected from the group
consisting of (1) flame retardant represented by formula (I),
wherein $\underline{a}$, $\underline{b}$, and $\underline{c}$ each independently represent an integer
of from 1 to 3; and at least one of by R_1, R_2, and R_3
represent an isopropyl group or an aryl group, the others of
R_1, R_2, and R_3 each independently represent a hydrogen atom or
a halogen-free alkyl group having from 1 to 30 carbon atoms,
which is not an isopropyl group, the total number of carbon
atoms in the substituents represented by R_1, R_2 and R_3 being

from 12 to 25 on an average in one molecule of the aromatic

phosphate, provided that said flame retardnat comprises a

plurality of aromatic phosphates having different

substituents, the total number of carbon atoms in the

5   substituents R_1, R_2 and R_3 of said flame retardant is

represented by a number average in the whole of the flame

retardant, which is the sum of the products of the weight

fraction of respective aromatic phosphate and the total

number of carbon atoms in the substituents in respective

10   aromatic phosphate, and (2) tris(nonylphenyl) phosphate

(wherein R_1, R_2 and R_3 in formula (I) each represent a nonyl

group) in an amount of from 3 to 30 parts by weight per 100

parts by weight of styrene resin used, wherein the total

content of aromatic vinyl monomers and dimerization and

15   trimerization products of aromatic vinyl monomers remaining

in the resin composition is not more than 1% by weight. The

flame retardant resin composition is preferably a dripping

flame retardant resin composition.

The flame retardant wherein at least one of the

20   substituents R_1, R_2 and R_3 is an isopropyl group may be a

flame retardant, the substituents of which are all alkyl

groups such as a nonylphenyl group but only one isopropyl

group or a flame retardant having from 4 to 8 isopropyl

groups in all so far as the total number of carbon atoms in

25   the substituents satisfies the foregoing requirements.

The flame retardant wherein at least one of the substituents R_1, R_2 and R_3 is an aryl group may be a flame retardant, the substituents of which are all alkyl groups such as nonylphenyl group but only one aryl group such as a

5   phenyl group, a benzyl group and a cumyl group or a flame retardant having a plurality of the foregoing aryl groups in all so far as the total number of carbon atoms in the substituents satisfies the foregoing requirements. Particularly preferred among the foregoing aryl groups are a

10   phenyl group, a benzyl group, and a cumyl group.

In the above preferred combination of the resin composition of the present invention, it is important that the total content of remaining aromatic vinyl monomers and dimerization and trimerization products of aromatic vinyl

15   monomers (hereinafter referrd to as remaining monomers and oligomers) in the resin composition not more than 1% by weight. The foregoing remaining monomers and oligomers acts as a fuel during combustion to deteriorate the flame retardance of the resin composition. The foregoing flame

20   retardant wherein at least one of R_1, R_2 and R_3 is selected from isopropyl group and/or aryl group, and tris(nonylphenyl) phosphate exhibit a volatility loss of not more than 50% by weight at a temperature of 400°C. The monomeric aromatic phosphate according to the main aspect of the present

25   invention such as bis(nonylphenyl)phenylphosphate has a volatility loss of not less than 50% by weight under the same

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conditions as mentioned above. In the dripping flame retardization mechanism, the flame retardance depends on the volatility loss of the flame retardance in gas phase. The flame retardant having a volatility loss of not less than 50% by weight at a temperature of 400°C exhibits an excellent flame retardance during combustion and thus does not show high dependence of flame retardance on the content of the foregoing remaining monomers and oligomers. However, the inventors have found a fact that among the flame retardants the aromatic phosphate, which has a low volatility at a temperature of 400°C, shows a great dependence of flame retardance on the content of the foregoing remaining monomers and oligomers and thus can be drastically improved in flame retardance when the content of the foregoing remaining monomers and oligomers falls below a predetermined value. This fact has heretofore been unknown and cannot even be foreseen from the conventional knowledge. While the reason for this mechanism is unknown, it is thought that a bulky group such as isopropyl group, a rigid group such as aryl group or a monomeric aromatic phosphate the total number of carbon atoms in the substituents of which exceeds 25 such as tris(nonylphenyl)phosphate has an extremely low volatility at a temperature of 400°C, causing the volatility loss of the foregoing remaining monomers and oligomers to exceed that of the foregoing flame retardant, and hence deteriorating the flame retardance of the resin composition.

From the standpoint of enhancement of heat resistance, another preferred combination constituting the low volatility flame retardant for styrene resin of the present invention is a dripping flame retardant resin

5   composition comprising a polyphenylene ether in an amount of from 1 to 10 parts by weight, preferably from 3 to 8 parts by weight, per 100 parts by weight of the styrene resin used, and a flame retardant selected from the group consisting of the foregoing flame retardants (1) and (2) in an amount of

10   from 1 to 20 parts by weight per 100 parts by weight of the styrene resin used, wherein the total content of aromatic vinyl monomer and dimerization and trimerization products of aromatic vinyl monomers remianing in the resin composition is not more than 1% by weight.

15   From the standpoint of provision of better dripping properties, a further preferred combination constituting the low volatility flame retardant for styrene resin of the present invention is a dripping flame retardant resin composition comprising a polyphenylene ether having a reduced

20   viscosity $\eta SP/C$ of from 0.3 to 0.6 dl/g in an amount of from 1 to 10 parts by weight, preferably from 3 to 8 parts by weight, per 100 parts by weight of a styrene resin which has a reduced viscosity $\eta SP/C$ of from 0.4 to 0.6 dl/g, and a flame retardant selected from the group consisting of the

25   foregoing flame retardants (1) and (2) in an amount of from 1 to 20 parts by weight per 100 parts by weight of the styrene

resin, wherein the total content of aromatic vinyl monomer and dimerization and trimerization products of aromatic vinyl monomers remaining in the resin composition is not more than 1% by weight.

Examples of the process for the preparation of the resin composition comprising the low volatility flame retardant for styrene resin of the present invention include a process which comprises melting a rubber-modified styrene resin and other thermoplastic resins, adding a flame retardant of the present invention to the resins, and then melt-kneading the mixture through the same extruder; and a process which comprises preparing a master batch comprising a styrene resin, other thermoplastic resins, and optionally a flame retardant of the present invention, and then kneading the master batch with the remainder of the styrene resin or the flame retardant of the present invention or other flame retardants.

In particular, as the preparation process using a polyphenylene ether as a thermoplastic resin, the following process is preferably employed.

One of the processes for the preparation of a resin composition comprising the low volatility flame retardant for styrene resin of the present invention and a polyphenylene ether as essential components comprises dividing a styrene resin into two batches, preparing a first resin composition comprising one of the two batches of the styrene resin and

a polyphenylene ether in an amount of not less than 50% by
weight based on the amount of the first resin composition,
melting the resin composition at a temperature of from 250°C
to 350°C in a former stage of a twin-screw extruder, and

5   melt-extruding the first resin composition with a second
resin composition comprising the others of the two batches of
the styrene resin and the flame retardants according to the
present invention at a temperature of from 200°C to 300°C in
a latter stage of the twin-screw extruder.

10   In the foregoing process, it is important that the
resin composition comprising a styrene resin and a
polyphenylene ether to be melted in the former stage of the
twin-screw extruder have a polyphenylene ether content of not
less than 50% by weight. If the polyphenylene ether content

15   falls below 50% by weight, no shearing force can be applied
to the resin composition, causing the production of unmolten
polyphenylene ether.

            It is preferred that the resin composition and the
flame retardant be separated from each other on melt-mixing

20   the resin composition. If the resin composition is melted in
the presence of the flame retardant, unmolten matters are
produced due to a great difference in viscosity between the
two components. In some detail, a resin composition
comprising a styrene resin and a polyphenylene ether having a

25   polyphenylene ether content of not less than 50% by weight is
melted at a temperature of from 250°C to 350°C.

Subsequently, the remainder of the resin composition and a flame retardant of the present invention are melted at a temperature of from 200°C to 300°C.

If the resin composition containing a polyphenylene ether is melted at a temperature of lower than 250°C, unmolten polyphenylene ether is produced. If the resin composition comprising a polyphenylene ether is melted at a temperature of higher than 350°C, the styrene resin begins to decompose. If the flame retardant of the present invention is melted at a temperature of lower than 200°C, the compatibility of the resin composition with the flame retardant is reduced, causing the phase separation of the flame retardant and hence making it difficult to perform stable extrusion. If the flame retardant is melted at a temperature of higher than 300°C, the flame retardant can disadvantageously evaporate or decompose.

In the process for the preparation of the resin composition comprising the low volatility flame retardant for styrene resin of the present invention, the twin-screw extruder preferably has L/D ratio of from 20 to 50, in which D represents the inner diameter of cylinder and L represents the length of screw, and a plurality of feed openings including a main feed opening and a side feed opening each disposed at different distances from the tip of the twin-screw extruder, kneading zones are provided between the plurality of feed openings and between the tip of the twin-

screw extruder and the feed opening nearest to the tip of the
twin-screw extruder, and the kneading zones each have a
length of from 3D to 10D.

Firstly, the foregoing L/D ratio is preferably from
20 to 50. If L/D falls below 20, it tends to give a poor
melt kneading, causing the production of unmolten
polyphenylene ether. If L/D exceeds 50, the retention time
of the resin composition in the extruder is prolonged,
possibly causing the deterioration of the resin composition.

Secondly, the twin-screw extruder preferably has two
or more feed openings having different distances from the tip
thereof. If there is only one feed opening, the
polyphenylene ether having a high melt viscosity and the
flame retardant of the present invention having a low melt
viscosity undergo phase separation. Thus, there are
preferably provided two or more feed openings. In some
detail, the resin composition is melted at the main feed
opening, followed by the feed of the flame retardant of the
present invention through the side feed openings.

Thirdly, there are preferably provided kneading zones
between the main feed opening and the side feed openings and
between the tip of the extruder and the side feed openings,
and the length of the kneading zones each is preferably from
3D to 10D. If the length of the kneading zones falls below
3D, it tends to give a poor melt kneading condition, causing
vent up or producing unmolten polyphenylene ether. If the

length of the kneading zones exceeds 10D, the retention time of the resin composition in the extruder is prolonged, deteriorating the resin composition. Further, in the case where there are provided a plurality of side feed openings, the kneading zones between the main feed opening and the side feed openings, between the different side feed openings, and between the tip of the extruder and the side feed openings need to satisfy the foregoing requirements.

Fourthly, the kneading zone of the twin-screw extruder is a zone for enhancing the kneading and mixing conditions. It comprises at least one of (1) full-flighted screw zone having a special mixing element, (2) reversed screw zone, and (3) mixing zone called kneading disc or kneading block.

The full-flighted screw zone having a special mixing element (1) comprises a mixing element such as Dulmage screw, fluted mixing element, uni-melt screw, spiral barrier screw, pin screw, pineapple mixer and cavity transfer mixer.

The reverse screw zone (2) is a zone which operates to suppress the resin flow and hence generate a back pressure, providing a great kneading capacity.

The mixing zone called kneading disc or kneading block (3) is a combination of ellipsoidal discs which are somewhat inclined to one another. A combination of ellipsoidal discs which are inclined to one another at 90° has no screwing force but has a good kneading capacity. A

combination of ellipsoidal discs which are inclined forward

to one another at 30° has some screwing force but has a small

kneading capacity. Further, the thickness of the discs can

be varied. The greater the thickness of the discs are, the

5   smaller is its mixing capacity but the better is its kneading

or shearing capacity. The greater the thickness of the discs

are, the greater are the screwing force and mixing capacity

but the small is the kneading capacity.

The shape of the kneading disc may be a triangular

10   triple-threaded disc or double-threaded disc. The triple-

threaded disc has a shallow groove that provides an excessive

shearing force but gives much opportunity of

branching/joining at intermeshed area to provide excellent

distribution and mixing properties. The double-threaded disc

15   has a smaller shearing force than the triple-thread disc.

The kneading disc can be controlled in its mixing and

kneading properties by varying the shape, angular position,

amount and thickness thereof.

Fifthly, the foregoing twin-screw extruder may be a

20   twin-screw unidirectional rotation extruder or twin-screw

bidirectional rotation extruder. The two screws may be non-

intermeshed, partially-intermeshed or fully-intermeshed. In

the case where a low shearing force is applied to obtain a

homogeneous resin at low temperatures, a bidirectional

25   rotation partially-intermeshed screw is preferred. In the

case where a certain great kneading force is required, a

unidirectional rotation fully-intermeshed screw is preferred. In the case where a greater kneading force is required, a unidirectional rotation fully-intermeshed screw is preferred.

The most desirable process for the preparation of the resin composition comprising the low volatility flame retardant for styrene resin of the present invention comprises preparing a master batch comprising a resin composition comprising a polyphenylene ether and a flame retardant of the present invention, or preparing a master batch comprising the foregoing resin composition as an essential component and a styrene resin and/or a rubber-modified styrene resin, adding to the master batch the remainder of the components of the final resin composition to form a mixture, and then melt-kneading the mixture, wherein the glass transition temperature (Tg) of the master batch is from 70°C to 100°C.

It is preferred that the foregoing master batch be prepared. If all the foregoing components are simultaneously melt-kneaded without preparing the foregoing master batch, or if a resin composition comprising a polyphenylene ether, a flame retardant, and a styrene resin or a resin composition comprising a polyphenylene ether or a flame retardant is melted by an extruder having a plurality of zones, subsequently followed by the melt-extrusion of the remainder of the styrene resin or a flame retardant, unmolten matter of polyphenylene ether having a high melt viscosity is produced

or a flame retardant which has easily undergone phase

separation is blown from the extruder, reducing the extrusion

stability. Thus, a polyphenylene ether having a high melt

viscosity, a flame retardant having a low melt viscosity, and

5   optionally a styrene resin can be used to produce a master

batch, giving a solution to the foregoing problems.

The glass transition temperature (Tg) of the

foregoing master batch is preferably from 70°C to 100°C. If

Tg exceeds 100°C, the master batch may not be thoroughly melt

10   in the presence of a styrene resin having a low melt

viscosity and a flame retardant, causing the production of

unmolten polyphenylene ether or the reduction of impact

strength. In particular, the impact strength depends on the

kneading conditions. On the contrary, if Tg falls below

15   70°C, the master batch can block the hopper or show a reduced

extrudability when fed to the extruder. Thus, the

preparation of the foregoing specific master batch makes it

possible to maintain sufficient extrusion stability and high

productivity and enhance impact strength, heat resistance,

20   melt flowability and external appearance even if the phase

separation of the flame retardant is suppressed to raise the

discharged amount in the subsequent melt extrusion.

A preferred example of the resin composition

comprising the low volatility flame retardant for styrene

25   resin of the present invention comprises a polyphenylene

ether (Component C), a monomeric alkyl-substituted aromatic

phosphate comprising NPDP, BNPP and TNPP (Component A) and a

polydimethylsiloxane (Component D) in an amount of from 3 to

8 parts by weight, from 3 to 8 parts by weight and from 0.1

to 2 parts by weight, respectively, based on 100 parts by

weight of a styrene resin (Component B) comprising from 30 to

70 parts by weight of a rubber-modified styrene resin and

from 30 to 70 parts by weight of an unmodified styrene resin.

The foregoing composition has an excellent balance of

flame retardance, particularly dripping flame retardance,

continuous molding properties, moldability (melt

flowability), impact strength, heat resistance and surface

hardness and water-resistant gloss retention of molded

product.

The resin composition comprising the low volatility

flame retardant for styrene resin of the present invention

can be obtained by subjecting the foregoing various

components to, e.g., melt kneading by means of a commercially

available single-screw extruder or twin-screw extruder.

During this procedure, to the system may be added an

oxidation inhibitor such as hindered phenol, an ultraviolet

absorbent such as benzotriazole and hindered amine, a tin

thermal stabilizer, an inorganic or halogenic flame

retardant, a lubricant such as stearic acid and zinc

stearate, a filler, a reinforcement such as glass fiber, a

colorant such as dye and pigment, etc. as necessary.

The composition thus obtained can be continuously

molded by means of an injection molding machine or extruder

for a prolonged period of time. The molded product thus

obtained is excellent in flame retardance (dripping flame

5   retardance), heat resistance and impact resistance.

<div align="center">Example</div>

The present invention will be further described in

the following examples and comparative examples, but the

present invention should not be construed as being limited

10   thereto.

In the following examples and comparative examples,

the various measurements were conducted by the following

measurement methods or measuring instruments:

(1) Analysis of flame retardant and resin composition

15   (A)   5 g of the resin composition was dissolved in

100 mℓ of methyl ethyl ketone, and then subjected to

separation by an ultracentrifugal separator (20,000 rpm, 1

hour). To the resulting supernatant liquid was then added

methanol in an amount of twice that of the supernatant liquid

20   to cause the resin component to separate out. The solution

portion and the resin portion were then separated from each

other by means of an ultracentrifugal separator. The

solution portion was then analyzed by GPC (gel permeation

chromatography) (available from Toso Co., Ltd. of Japan;

25   chromatography apparatus (equipped with RI refractive index

detector): HLC-8020; column: available from Toso Co., Ltd.;

G1000HXL (2 sets used); mobile phase: tetrahydrofuran; flow
rate: 0.8 mℓ/min.; pressure: 60kgf/cm^2; temperature: 35°C
(inlet), 40°C (oven), 35°C (RI); sample loop: 100 mℓ;
injected amount of sample: 0.08 g/20mℓ). Supposing that the
area ratio of the various components on chromatography are
the weight fraction of the various components, the
composition and content of the phosphate and dimerization and
trimerization products of remaining aromatic vinyl monomer
and aromatic vinyl monomer were determined from these area
ratios. The resin portion was measured for the ratio of
integrated value of aromatic proton or aliphatic proton by
means of a Fourier transformation nuclear magnetic resonance
apparatus (proton-FT-NMR). Thus, the amount of the rubber-
modified or unmodified styrene resins and the thermoplastic
resin such as aromatic polycarbonate and polyphenylene ether
were determined.

(B) Acid value of flame retardant

The flame retardant was measured for acid value in
accordance with JIS-K6751 as a measure of the amount of
remaining acidic substances therein.

(C) Color hue of flame retardant

The flame retardant was measured for color hue by
Gardner process in accordance with "Reference Fats and Oils
Analysis Method" established by Society of Oil Chemistry of
Japan. The smaller the value of Gardner standard color is,
the thinner is the color hue.

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(D) Light resistance of flame retardant

For the evaluation of light resistance, 30 g of the flame retardant was charged in a 50-mℓ vial. The sample was then allowed to stand in SUN TESTER XF-180 (light source: xenon lamp) available from Shimadzu Corp. for 10 days. The percent change in color hue and acid value from before to after the test was determined as an index of light resistance.

(E) Thermal discoloration resistance of flame retardant

For the evaluation of thermal discoloration resistance, 30 g of the flame retardant was charged in a 50-mℓ vial. The sample was then allowed to stand at a temperature of 300°C for 1 hour. The percent change in color hue was then determined as an index of thermal discoloration resistance.

(F) Viscosity of flame retardant

The flame retardant was measured for viscosity at a temperature of 25°C by means of a Brookfield type viscometer available from Brookfield Engineering Laboratories, Inc. (Stoughton, Massachusettes, USA).

(G) Residual amount of aluminum, magnesium, sodium and antimony in flame retardant

In order to determine the residual amount of aluminum, magnesium, sodium and antimony in the flame retardant, the flame retardant was analyzed by atomic

absorption spectroscopy as described in "Encyclopedia of
Chemical Technology", Third Edition, Volume 2, 'Atomic
Absorption and Emission Spectroscopy', pp. 621 - 623, 591,
155, 156, A Wiley-Interscience Publication, John Wiley &
5   Sons, New York, 1978.

   (H)   Volatility of flame retardant

   The flame retardant was heated at a rate of 40°C/min.
in a stream of nitrogen by means of a Type DT-40 thermal
analyzer available from Shimadzu Corp. of Japan. The weight
10   loss at 300°C or 400°C was determined as a measure of
volatility (thermogravimetric analysis test: TGA method).

   The flame retardant was allowed to stand at a
temperature of 250°C for 5 minutes in a stream of nitrogen by
means of the same apparatus as mentioned above. The
15   resulting residual amount was determined as another measure
of volatility.

   (2) Weight-average particle diameter of rubber-modified
styrene resin

   For the measurement of the weight-average particle
20   diameter of the rubber-modified styrene resin, the diameter
of rubber particles (butadiene polymer particles) on a
transmission electron micrograph of an ultrathin section of
the resin composition was determined. The weight-average
particle diameter of the rubber-modified styrene resin was
25   calculated from the following equation:

Weight-average particle diameter = $\Sigma Ni \cdot Di4 / \Sigma Ni \cdot Di3$

(wherein Di represents measured particle diameter of butadiene polymer particles, and Ni represents the number of measured butadiene polymer particles having a particle diameter of Di)

(3) Reduced viscosity $\eta SP/C$ of rubber-modified styrene resin and polyphenylene ether

To 1g of the rubber-modified styrene resin was added a mixture of 18 mℓ of methyl ethyl ketone and 2 mℓ of methanol. The mixture was then shaken at a temperature of 25°C for 2 hours. The mixture was then subjected to centrifugal separation at a temperature of 5°C at 18,000 rpm for 30 minutes. The resulting supernatant liquid was then withdrawn. The resin content was precipitated with methanol, and then dried.

0.1 g of the resin thus obtained was dissolved in toluene for a rubber-modified polystyrene resin, or in methyl ethyl ketone for a rubber-modified acrylonitrile-styrene copolymer resin, to make a 0.5 g/dl solution. 10 mℓ of the solution thus obtained was then charged in a Cannon-Fenske viscometer. The solution was then measured for dropping time T_1 (second) at a temperature of 30°C. Pure toluene or pure methyl ethyl ketone was measured for dropping time T_0 (second) by means of the same viscometer. The reduced viscosity $\eta SP/C$ was then calculated from the following

equation in which C represents the resin concentration (g/dl):

$$\eta SP/C = (T_1/T_0 - 1)/C$$

For the evaluation of the reduced visocosity $\eta SP/C$ of the polyphenylene ether, 0.1 g of the polyphenylene ether was dissolved in chloroform to make a 0.5 g/dl solution which was then measured in the same manner as described above.

(4) Izod impact strength

Izod impact strength was measured at a temperature of 23°C in accordance with ASTM-D256 with a V-notch and a 1/8-inch test piece.

(5) Dart impact strength

Dart impact strength was measured at a temperature of 23°C by a method similar to ASTM-D1709. Specifically, a Du Pont impact tester (available from Toyo Seiki Seisakujo K.K.) was used. A dart (weight: 200 g) having a diameter of 9.5 mm at the tip of impact center and a length of 5.2 mm was brought into contact with the surface of a molded product (70 mm square; 2 mm thick) on a pad having a diameter of 9.5 mm and a hole depth of 4.0 mm. A load was dropped onto the molded product from a height of 50 cm at maximum. The weight of the load under which 50% of the molded product is destroyed was defined as 50% destruction load. 50% destruction load was then multiplied by the weight of the

dropping load to calculate 50% destruction energy as dart

impact strength. (unit: kgcm)

(6) Rigidity

Flexural modulus was measured in accordance with

ASTM-D790 as a.measure of rigidity.

(7) Tensile strength and tensile elongation

Tensile strength and tensile elongation were measured

in accordance with ASTM-D638.

(8) Heat distortion temperature

Heat distortion temperature was measured in

accordance with ASTM-D648 as a measure of heat resistance.

(Test load: 18.5 Kg/cm^2; 1/4 inch-thick test piece)

(9) Vicat softening temperature

Vicat softening temperature was measured in

accordance with ASTM-D1525 as a measure of heat resistance.

(10) Melt flow rate (MFR)

Melt flow rate was measured in accordance with ASTM-

D1238 as an index of melt flow. The extruding rate per 10

minutes (g/10min) at a load of 5 kg and a melting temperature

of 200°C was determined.

(11) Gloss

For the evaluation of gloss, the specular gloss at an

incidence angle of 60 degrees was determined in accordance

with ASTM-D523.

(12) Flame retardance

Flame retardance was evaluated by VB (Vertical Burning) method in accordance with UL-subject 94 by using a 1/8-inch test piece.

For the details of the method described in UL-subject 94, reference can be made to e.g., U.S. Patent 4,966,814.

Heat release rate was measured using ATLAS Cone Calorimeter II available from ATLAS Electric Devices Co. of USA in accordance with ASTM-E1354. The measurement was conducted at a radiant heat flux of 50 kW/m^2. The sample was installed horizontally. The area of the sample was 0.006 m^2.

(13) Volatility of resin composition (thermogravimetric analysis test: TGA method)

The resin composition was heated at a rate of 10°C/min in a stream of nitrogen by means of a Type DT-40 thermal analyzer available from Shimadzu Corp. of Japan. The temperature at which the weight loss reaches 1% was determined as a measure of the volatility of the resin composition.

(14) Light resistance of molded product

Light resistance test was conducted using ATLAS C135W Weatherometer available from ATLAS Electric Devices Co. of USA as a light resistance tester in accordance with JIS K7102. The sample was irradiated with xenon light (wavelength: 340 nm; energy: 0.30 W/m^2) at a tester internal temperature of 55°C and a humidity of 55% without shower for

300 hours. The color difference ΔE from before to after the test was determined by L.a.b. method using a Type SM-3 SM color computer available from Suga Shikenki Co., Ltd. of Japan to evaluate the tone change. The smaller the color

5   difference is, the higher is the light resistance.

(15) Percent heat shrinkage of molded product of resin composition

A 1/8-inch thick molded product of resin composition obtained by compression molding or injection molding was

10   allowed to stand in a 170°C hot-air drier for 15 minutes. Percent heat shrinkage S (%) was then calculated from the dimensional change of the molded product by the following equation:

$$S = (L_0 - L) \times 100/L_0$$

15   (wherein L_0 represents the size before heating, and L represents the size after heating)

(16) Water-resistant gloss retention of molded product

For the evaluation of water resistance, the molded product was allowed to stand in a 80°C constant temperature

20   water for 24 hours. The gloss change (ΔG) from before to after the test was determined as an index of water resistance. The smaller ΔG is, the smaller is the gloss change by hot water.

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<u>(17) Surface hardness of molded product</u>

The molded product was measured for pencil hardness (pencil scratch value) in accordance with JIS-K5400 as an index of the surface hardness of the molded product.

<u>(18) Kneadability</u>

The following parameters were used to evaluate kneadability.

$$\text{Kneadability parameter} = \frac{\text{(Extrusion factor)}}{\text{(circumferential speed of screw)}}$$

$$= (Q/D^2)/\pi ND$$

wherein Q represents the extrusion (kg/hr); N represents the number of revolutions of screw (rpm); and D represents the inner diameter of cylinder (mm).

<u>(19) Glass transition temperature (Tg)</u>

The sample was heated to a temperature of 400°C at a rate of 10°C/min in a stream of nitrogen by means of a Type DT-40 thermal analyzer available from Shimadzu Corp. Glass transition temperature was measured by DSC method.

As the various components to be used in the examples and comparative examples, the following compounds were used.

(a)   Aromatic phosphate (Component A)

(1)   Triphenyl phosphate (TPP)

        A commercial aromatic phosphate (trade name: TPP
(hereinafter referred to "TPP"), available from Daihachi
Kagaku Kogyo Co., Ltd.) was used.

        The total number of carbon atoms in the substituents
of TPP was 0 on the average, and the phosphorus content was
9.5% by weight.

(2)   Oligomeric aromatic phosphate (fr-1)

        A commercial oligomeric aromatic phosphate derived
from bisphenol A (trade name: CR741 (hereinafter referred to
as "fr-1"), available from Daihachi Kagaku Kogyo Co., Ltd.)
was used. According to GPC analysis, the oligomeric aromatic
phosphate comprises TPP-A-dimer (n=1) and TPP-A-oligomer
(n≥2) represented by the following formula and triphenyl
phosphate (TPP) in a weight proportion of 84.7/13.02/2.3.
The phosphorus content was 9.4% by weight.
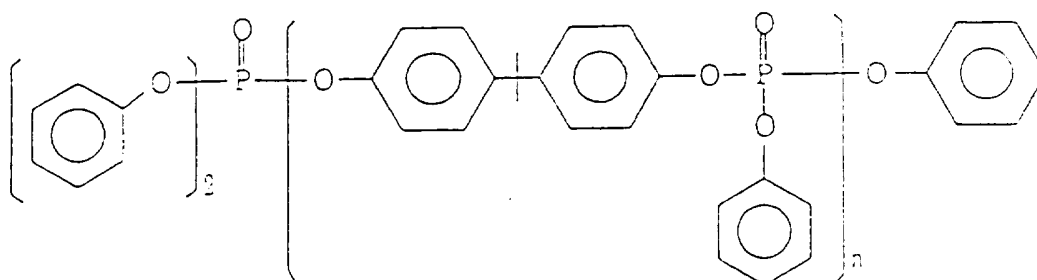
(3)   Preparation of monomeric alkyl group-substituted aromatic phosphate (FR-1)

287.3 parts by weight (molar ratio: 2.0) of nonylphenol and 0.87 parts by weight (molar ratio: 0.01) of aluminum chloride were measured out in a flask. 100 parts by weight (molar ratio: 1.0) of phosphorus oxychloride were then added dropwise to the mixture at a temperature of 90°C in 1 hour. To the resulting intermediate product were then added 61.4 parts by weight (molar ratio: 1.0) of phenol to cause further reaction. In order to complete the reaction, the reaction system was gradually heated eventually to 180°C to complete esterification. The resulting reaction product was cooled, and then washed with water so that the catalyst and chlorine content were removed to obtain a phosphate mixture (hereinafter referred to as "FR-1"). The mixture thus obtained was then analyzed by GPC (gel permeation chromatography; HLC-8020 available from Toso Co., Ltd. (mobile phase: tetrahydrofuran)). As a result, it was found that the mixture comprises bis(nonylphenyl)phenylphosphate (hereinafter referred to as "BNPP"), trisnonylphenyl phosphate (hereinafter referred to as "TNPP"), nonylphenyl diphenyl phosphate (hereinafter referred to as "NDPP"), and nonylphenol in a weight proportion of 77.8/11.3/8.4/2.5.

The total number of carbon atoms in the substituents was 17.9 on the average ($18 \times 0.778 + 27 \times 0.113 + 9 \times 0.084 = 17.9$), and the phosphorus content was 5.5% by weight.

The monomeric aromatic phosphate mixture (FR-1) was

distilled, and then fractionated by liquid chromatography to

obtain BNPP.

(4) Preparation of various monomeric alkyl-

5   substituted aromatic phosphates

The procedure of FR-1 preparation was followed except

that commercial alkylphenols or various alkylphenols obtained

by the method described in "ENCYCLOPEDIA OF CHEMICAL

TECHNOLOGY", Third Edition, Volume 2, 'ALKYLPHENOLS',

10   p. 72 - 96 (A WILEY-INTERSCIENCE PUBLICATION, John Wiley &

Sons, New York 1978) were used with their molar ratio to

phosphorus oxychloride being controlled to synthesize various

alkylphenols. The purification of these alkylphenols was

effected by the foregoing rinsing, distillation or

15   fractionating by liquid chromatography. Table 1 shows the

various alkylphenols.

(b) Thermoplastic resin

(1) Rubber-modified styrene resin (HIPS)

A polybutadiene ((cis-1,4 bond/trans-1,4 bond/vinyl-

20   1,2 bond weight ratio = 95/2/3); trade name: Nipol 122 OSL,

available from Nihon Zeon Co., Ltd.) was dissolved in the

following mixture to make a homogeneous solution.

Polybutadiene	10.5% by weight
Styrene	74.2% by weight
Ethylbenzene	15.0% by weight
α-Methylstyrene dimerization product	0.27% by weight
t-Butylperoxyisopropyl carbonate	0.03% by weight

The foregoing mixture was continuously supplied into an agitated serial 4-stage reactor. Thus, the mixture was allowed to undergo polymerization at an agitation rate of 190 rpm and a temperature of 126°C in the 1st stage, at an agitation rate of 50 rpm and a temperature of 133°C in the 2nd stage, at an agitation rate of 20 rpm and a temperature of 140°C in the 3rd stage, and then at an agitation rate of 20 rpm and a temperature of 155°C in the 4th stage. Subsequently, the resulting polymerization solution having a solid content of 73% was introduced into a devolatilizing apparatus wherein the unreacted monomers and the solvent were then removed to obtain a rubber-modified styrene resin (hereinafter referred to as "HIPS-1"). The rubber-modified styrene resin thus obtained was then analyzed. As a result, it was found that the rubber-modified styrene resin exhibits a rubber content of 12.1% by weight, a weight-average particle diameter of 1.5 μm and a reduced viscosity ηSP/C of 0.53 dl/g.

The amount of polymerization initiator and chain transfer agent and polymerization temperature were varied to prepare rubber-modified styrene resins having different reduced viscosities ηSP/C. The results are set forth in

5   Table 8.

Further, various HIPS having different rubber kinds, rubber contents, rubber weight-average particle diameters and reduced viscosities ηSP/C were prepared. In some detail, the foregoing procedure was followed except that a styrene-

10   butadiene block copolymer (styrene/butadiene ratio = 40/60 (by weight), cis-1,4 bond/trans-1,4 bond/vinyl-1,2 bond weight ratio = 37/50/13)) was used as a rubber instead of the foregoing butadiene and the agitation rate was altered to control the weight-average particle diameter of rubber and

15   the amount of α-methylstyrene dimerization product was altered to control the reduced viscosity of the product. The HIPS's thus obtained exhibited a rubber content of 15.0% by weight, a rubber weight-average particle diameter of 0.34 μm and a reduced viscosity ηSP/C of 0.68 dl/g (hereinafter

20   referred to as "HIPS-7").

The production procedure of HIPS-1 was followed except that part of styrene was replaced by α-methylstyrene or butyl acrylate to prepare a copolymer HIPS (hereinafter referred to as "MS-HIPS" and "BA-HIPS", respectively). The

25   copolymerizable monomer (α-methylstyrene or butyl acrylate) content of MS-HIPS and BA-HIPS was 4% by weight.

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(2) Rubber-unmodified styrene resin

A mixture of 80.0 parts by weight of styrene, 20 parts by weight of ethylbenzene, and 0.03 parts by weight of 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane as an initiator was continuously supplied into a coil type full-mixed reactor at a rate of 2.5 ℓ/hr. so that the reaction mixture was allowed to undergo polymerization at a temperature of 150°C for an average retention time of 2 hours with a polymer solid concentration of 48%. Subsequently, the polymerization solution was introduced into a 230°C devolatilizing apparatus where the unreacted monomers and the solvent were removed to obtain a polystyrene. The polystyrene thus obtained exhibited a weight-average molecular weight of 160,000 and a number-average molecular weight of 76,000 (hereinafter referred to as "GPPS-2").

The foregoing procedure was followed except that n-dodecyl mercaptan was added as a chain transfer agent or the polymerization temperature was raised to prepare polystyrenes having lower molecular weights. The results are set forth in Tables 9 and 12.

(3) Rubber-unmodified copolymer styrene resin

A mixture of 78.0 parts by weight of styrene, 2.0 parts by weight of methacrylic acid, 20 parts by weight of ethylbenzene, 0.02 parts by weight of n-dodecyl mercaptan, and 0.03 parts by weight of 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane as an initiator was continuously

supplied into a coil type complete mixing reactor at a rate
of 2.5 ℓ/hr. so that the reaction mixture was allowed to
undergo polymerization at a temperature of 150°C for an
average retention time of 2 hours with a polymer solid

5   concentration of 47%. Subsequently, the polymerization
solution was introduced into a 230°C devolatizing apparatus
where the unreacted monomers and the solvent were removed to
obtain a styrene-methacrylic acid copolymer. The copolymer
thus obtained exhibited a styrene/methacrylic acid weight

10   ratio of 96/4, a weight-average molecular weight of 120,000
and a number-average molecular weight of 63,000 (hereinafter
referred to as "SMAA-3").

       The foregoing procedure was followed except that
methacrylic acid, maleic anhydride, α-methylstyrene, or butyl

15   acrylate was used as a copolymerizable monomer and the amount
of ethylbenzene as a solvent was reduced or the
polymerization temperature was raised to prepare copolymers
having higher molecular weights. The foregoing procedure was
followed except that the amount of n-dodecyl mercaptan used

20   as a chain transfer agent was increased or the polymerization
temperature was raised to prepare copolymers having lower
molecular weights. Further, the ratio of components to be
charged for polymerization was altered to control the
polymerization composition ratio. The results are set forth

25   in Table 9.

(4) Preparation of polyphenylene ether (PPE)

The interior of a stainless steel reactor having an oxygen blowing port at the bottom thereof and a cooling coil and an agitating blade thereinside was thoroughly replaced by nitrogen. 54.8 g of cupric bromide, 1,110 g of di-n-butylamine, and a solution of a 8.75 kg of 2,6-xylenol in a mixture of 20 ℓ of toluene, 16 ℓ of n-butanol and 4 ℓ of methanol were then charged into the reactor. The reaction mixture was then allowed to undergo polymerization with stirring with oxygen being blown into the reactor while the internal temperature was being controlled to 30°C for 90 minutes. After the completion of the polymerization, the polymer which had separated out was withdrawn by filtration. To the polymer thus obtained was then added a methanol/hydrochloric acid mixture to decompose the remaining catalyst in the polymer. The polymer was thoroughly washed with methanol, and then dried to obtain a powdered polyphenylene ether (hereinafter referred to as "PPE-1"). The product showed a reduced viscosity ηSP of 0.41 dl/g.

The foregoing procedure was followed except that the amount of the catalyst to be used or the polymerization time was controlled during the preparation of polyphenylene ether to prepare polyphenylene ethers having different reduced viscosities ηSP/C. The results are set forth in Table 10.

(5)   Aromatic polycarbonate (PC)

A commercial bisphenol A type polycarbonate (Novalex 8025A, available from Mitsubishi Chemical Corp. of Japan) (hereinafter occasionally referred to as "PC") was used.

5
(6)   ABS resin (ABS)

A commercial ABS resin (acrylonitrile/butadiene/ styrene = 26/14/60 (by weight)) (hereinafter occasionally referred to as "ABS") was used.

(7)   Polyethylene (PE)

10
A commercial low density polyethylene was used.

(8)   Polypropylene (PP)

A commercial unmodified polypropylene was used.

(9)   Polyamide (PA)

A commercial polyamide 6 was used.

15
(10)   Polyethylene terephthalate (PET)

A commercial polyethylene terephthalate was used.

(c)   Polyorganosiloxane

Polydimethylsiloxanes having different kinematic viscosities (Shin-Etsu silicone KF96 series, available from

20
Shin-Etsu Chemical Co., Ltd.) were used as shown in Table 16.

(d)   Light resistance improver

(1)   Ultraviolet light absorber

A benzotriazole ultraviolet light absorber available from Ciba Geigy Corp. (trade name: Tinuvin P (hereinafter

25
referred to as "UVA")) was used.

(2)   Hindered piperidine light stabilizer

A hindered piperidine light stabilizer available from Ciba Geigy Corp. (trade name: Tinuvin 770 (hereinafter referred to as "HALS") was used.

(3)   Sunproofing agent

A commercial titanium oxide (TiO_2) powder (available from Ishihara Sangyo Kaisha, Ltd.; average size: 0.2 μm (hereinafter referred to as "TiO_2") was used.

(4)   Antioxidant

An antioxidant available from Ciba Geigy Corp. (trade name: Irganox 1076 (hereinafter referred to as "AO")) was used.

(e) Flame retardant

(1)   A tetrabromobisphenol A epoxy oligomer (hereinafter referred to as "BEO") was used as a halogenated bisphenol type epoxy resin.

(2)   Antimony trioxide

A commercial antimony trioxide (hereinafter referred to as "Sb_2O_3") was used as an auxiliary flame retardant.

The styrene resins used in the following examples, comparative examples and tables are abbreviated as follows:

HIPS: Rubber-modified polystyrene

HIPS-1: Polybutadiene rubber-modified polystyrene having a rubber content of 12.1% by weight, a rubber weight-average particle diameter of 1.5 μm and a reduced viscosity ηSP/C of 0.53 dl/g

HIPS-2: Polybutadiene rubber-modified polystyrene having a rubber content of 12.1% by weight, a rubber weight-average particle diameter of 1.5 μm and a reduced viscosity ηSP/C of 0.79 dl/g

5   HIPS-3: Polybutadiene rubber-modified polystyrene having a rubber content of 12.1% by weight, a rubber weight-average particle diameter of 1.5 μm and a reduced viscosity ηSP/C of 0.60 dl/g

HIPS-4: Polybutadiene rubber-modified polystyrene

10   having a rubber content of 12.1% by weight, a rubber weight-average particle diameter of 1.5 μm and a reduced viscosity ηSP/C of 0.58 dl/g

HIPS-5: Polybutadiene rubber-modified polystyrene having a rubber content of 12.1% by weight, a rubber weight-

15   average particle diameter of 1.5 μm and a reduced viscosity ηSP/C of 0.40 dl/g

HIPS-6: Polybutadiene rubber-modified polystyrene having a rubber content of 12.1% by weight, a rubber weight-average particle diameter of 1.5 μm and a reduced viscosity

20   ηSP/C of 0.35 dl/g

HIPS-7: Styrene-butadiene rubber (styrene/butadiene ratio = 40/60 (by weight))-modified polystyrene having a rubber content of 15.0% by weight, a rubber weight-average particle diameter of 0.3 μm and a reduced viscosity ηSP/C of

25   0.68 dl/g

GPPS: Rubber-unmodified polystyrene

GPPS-1: Rubber-unmodified polystyrene having a weight-average molecular weight of 212,000 and a number-average molecular weight of 87,000

GPPS-2: Rubber-unmodified polystyrene having a weight-average molecular weight of 160,000 and a number-average molecular weight of 76,000

GPPS-3: Rubber-unmodified polystyrene having a weight-average molecular weight of 135,000 and a number-average molecular weight of 71,000

GPPS-4: Rubber-unmodified polystyrene having a weight-average molecular weight of 101,000 and a number-average molecular weight of 59,000

SMAA: Styrene-methacrylic acid copolymer

SMAA-1: Styrene/methacrylic acid = 92/8 (by weight)
Weight-average molecular weight: 200,000;
Number-average molecular weight: 85,000

SMAA-2: Styrene/methacrylic acid = 93/7 (by weight)
Weight-average molecular weight: 110,000;
Number-average molecular weight: 55,000

SMAA-3: Styrene/methacrylic acid = 96/4 (by weight)
Weight-average molecular weight: 122,000;
Number-average molecular weight: 63,000

SMA: Styrene-maleic anhydride

        SMA-1: Styrene/maleic anhydride = 92/8 (by weight)

              Weight-average molecular weight: 248,000;

              Number-average molecular weight: 113,000

5   SMA-2: Styrene/maleic anhydride = 85/15 (by weight)

              Weight-average molecular weight: 203,000;

              Number-average molecular weight: 97,000

<div align="center">

EXAMPLES 1 TO 5 AND
COMPARATIVE EXAMPLES 1 TO 6

</div>

10   The various monomeric aromatic phosphates set forth in Table 1 were allowed to stand at a temperature of 250°C in a stream of nitrogen for 5 minutes, and then measured for residual amount by thermogravimetric analysis test. The results are set forth in Table 1 and Fig. 1. Table 1 and

15   Fig. 1 show that the monomeric aromatic phosphates wherein the total number of carbon atoms in the substituents R_1, R_2 and R_3 is not less than 12 on the average as a whole exhibit an excellent non-volatility.

Table 1

Monomeric alkyl group-substituted aromatic phosphate

Example No.	Total number of carbon atoms in substituents	Designation	Non-volatility Remaining amount after 5 minutes of 250°C storage
Comparative Example 1	0	TPP: Triphenyl phosphate	14
Comparative Example 2	3	TCP: Tricresyl phosphate	52
Comparative Example 3	6	TXP: Trixylenyl phosphate	65
Comparative Example 4	9	NPDP: Nonylphenyl diphenyl phosphate	75
Example 1	12	DPDP: Dodecylphenyl diphenyl phosphate	95
Example 2	15	PDDP: Pentadecyl diphenyl phosphate	96
Example 3	18	BNPP: Bis(nonylphenyl)phenyl phosphate	96
Example 4	20	ODDP: Octadecylphenyl diphenyl phosphate	96
Example 5	25	BONP: Bis(octylphenyl)nonylphenyl phosphate	97
Comparative Example 5	27	TNPP: Tris(nonylphenyl) phosphate	97
Comparative Example 6	30	BNDP: Bis(nonylphenyl)dodecylphenyl phosphate	97

EXAMPLES 6 TO 10 AND
COMPARATIVE EXAMPLES 7 TO 13

HIPS-1, GPPS-1 and the aromatic phosphates set forth
in Table 2 were mechanically mixed in a proportion of 70/30/7
(by weight). The mixtures were each then melted at a
temperature of 220°C at 50 rpm for 5 minutes in a
laboplastomill available from Toyo Seiki Seisakujo K.K. The
resin compositions thus obtained were each then subjected to
compression molding to prepare 1/8-inch thick specimens to be
evaluated for flame retardance. The specimens thus obtained
were each then measured for the total content of the
remaining styrene monomer and dimerization and trimerization
products of styrene (remaining monomers and ologomers) in
accordance with the measuring method described above. As a
result, the foregoing remaining monomers and oligomers were
detected in an amount of from 1.1 to 1.5% by weight in all
the specimens. Further, TPP, fr-1, and BNPP were each heated
at a rate of 40°C/min in a stream of nitrogen. The
relationship between temperature and weight loss was
determined by thermogravimetric analysis test. The results
are set forth in Table 2 and Fig. 2.

Table 2 and Fig. 2 show that the specimens wherein
the total number of carbon atoms in the substituents of
aromatic phosphate is from 12 to 25 on the average exhibit an
excellent balance between flame retardance and non-
volatility.

As compared with the monomeric aromatic phosphate,
the oligomeric aromatic phosphate exhibits a small volatility
at 400°C in the initial stage of combustion and hence
deteriorated flame retardance. Further, the specific

5　　　monomeric alkyl group-substituted aromatic phosphate stays
non-volatile at a molding temperature of not higher than
300°C and evaporates effectively in the initial stage of
combustion, providing an excellent flame retardance.

Table 2

Monomeric alkyl group-substituted aromatic phosphate

Example No.	Total number of carbon atoms in substituents	Name	Weight loss (TGA method)		Flame retardance		
			300°C	400°C	Average flame-out time(sec.)	Dripping of flaming particles	UL 94 judgement
Comparative Example 7	0	TPP	32	100	14	Yes	V-2
Comparative Example 8	3	TCP	29	100	13	Yes	V-2
Comparative Example 9	6	TXP	23	100	13	Yes	V-2
Comparative Example 10	9	NPDP	18	95	13	Yes	V-2
Example 6	12	DPDP	13	83	13	Yes	V-2
Example 7	15	PDDP	8	78	13	Yes	V-2
Example 8	18	BMPP	3	65	14	Yes	V-2
Example 9	20	ODDP	3	60	14	Yes	V-2
Example 10	25	BONP	3	52	15	Yes	V-2
Comparative Example 11	27	TNPP	2	23	28	Yes	HB*
Comparative Example 12	30	BNDP	1	15	41	Yes	HB*
Comparative Example 13	Oligomeric phosphate	fr-1	3	8	40	Yes	HB*

*HB: Rank which does not belong to any one of V-0, V-1 and V-2 when evaluated for flame retardance in acccordance with UL-94 (hereinafter the same)

V-2: Undergoes flame-out due to melt dripping after ignition when evaluated for flame retardance in accordance with UL-94 (hereinafter the same)

EXAMPLES 11 TO 14 AND
COMPARATIVE EXAMPLES 14 TO 17

A resin compositions set forth in Table 3 and BNPP were processed in the same manner as in Example 6 to prepare specimens to be evaluated for flame retardance. The results are set forth in Table 3. The specimens thus obtained were each measured for the total content of the remaining styrene monomer and dimerization and trimerization products of styrene in accordance with the measuring method described above. As a result, the foregoing remaining monomers and ologomers were detected in an amount of from 1.1 to 1.5% by weight in all the specimens.

Table 3

Example No.	Resin composition (weight ratio)		Compatibility during melt kneading	Flame retardance (self-dripping flame-out)		
	Resin	BNPP		Average flame-out time (sec.)	Dripping of flaming particles	UL-94 judgement
Comparative Example 14	PE 100	7	Phase separation	≥60	Yes	HB*
Comparative Example 15	PP 100	7	Phase separation	≥60	Yes	HB*
Comparative Example 16	PA 100	7	Good	50	Yes	HB*
Comparative Example 17	PET 100	7	Phase separation	55	Yes	HB*
Example 11	HIPS-1 100 PE 12	7	Good	20	Yes	V-2
Example 12	HIPS-1 100 PP 12	7	Good	21	Yes	V-2
Example 13	HIPS-1 100 PA 12	7	Good	15	Yes	V-2
Example 14	HIPS-1 100 PET 12	7	Good	16	Yes	V-2

EXAMPLES 15 TO 18 AND
COMPARATIVE EXAMPLES 18 TO 25

A composition obtained by compounding the aromatic
phosphate set forth in Table 4 with 100 parts by weight of a
5   styrene resin comprising 70/30 mixture of HIPS-1 and GPPS-1
was processed in the same manner as in Example 6 to prepare
specimens to be evaluated for MFR, Izod impact strength,
Vicat softening temperature and flame retardance. The
results are set forth in Table 4 and Figs. 3 and 4. The
10   specimens thus obtained were each measured for the total
content of the remaining styrene monomer and dimerization and
trimerization products of styrene in accordance with the
measuring method described above. As a result, the foregoing
remaining monomers and oligomers were detected in an amount
15   of from 1.1 to 1.5% by weight in all the specimens.

Table 4 and Figs. 3 and 4 show that the aromatic
phosphate of the present invention (BNPP) exhibits an
excellent balance between flame retardance and physical
properties while TNPP and the oligomeric aromatic phosphate
20   (fr-1) provides a reduced flame retardance when used in the
same amount as BNPP and reduced heat resistance and impact
strength when used in a greater amount.

Table 4

	Examples				Comparative Examples						
	15	16#	17#	18	19	20	21	22	23	24	25
Resin composition											
HIPS-1	70	70	70	70	70	70	70	70	70	70	70
GPPS-1	30	30	30	30	30	30	30	30	30	30	30
Aromatic phosphate	BNPP(bis(nonylphenyl)phosphate)				TNPP(tris(nonylphenyl)phosphate)			fr-1(oligomeric aromatic phosphate)			
Add parts by weight	3	5	6	8	5	6	8	3	5	6	8
Evaluation of molded product											
Flame retardance											
Average flame-out time (sec.)	25	20	16	8	40	36	26	69	51	42	29
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	HB*	HB*	HB*	HB*	HB*	HB*	HB*
MFR (g/10 min)	10.1	11.8	14.0	18.4	10.5	12.0	14.9	6.9	10.0	11.2	13.9
Izod impact strength (kgcm/cm)	9.3	8.7	8.4	7.8	8.6	8.2	7.5	8.8	8.1	7.8	7.0
Vicat softening temperature (°C)	101	96	94	89	97	95	90	103	98	96	91

#: Indicates preferred examples (hereinafter the same)

*: (hereinafter the same)

EXAMPLES 19 AND 20 AND
COMPARATIVE EXAMPLES 26 AND 27

   The monomeric aromatic phosphates set forth in Table
5 were each examined for light resistance in accordance with
the testing method described above. The results are set
forth in Table 5.

   Table 5 shows that the monomeric aromatic phosphate
containing isopropyl group exhibits a high viscosity and
shows a great color hue and acid value change in the light
resistance test.

Table 5

Example No.	Total number of carbon atoms in substituents	Monomeric alkyl group-substituted aromatic phosphate Name	25°C viscosity (CS)	% Change from before to after light resistance test		
				Color hue (Gardner)	Acid value (mgKOH/g)	Thermal discoloration (300°C, 1 hr.)
Example 19	18	Bis(nonylphenyl)phenyl phosphate	1,900	250	16	300
Comparative Example 26	18	Tris(diisopropylphenyl) phosphate	18,000	5,000	257	6,000
Comparative Example 27	18	Tris(phenylphenyl) phosphate	15,000	3,500	160	4,600
Example 20	16	Bis(isobutylphenyl)-diisobutylphenyl phosphate	7,000	300	51	450

<u>EXAMPLES 21 TO 23 AND</u>
<u>COMPARATIVE EXAMPLES 28 AND 29</u>

A composition obtained by compounding the aromatic phosphate set forth in Table 6 with 100 parts by weight of a styrene resin comprising 70/30 mixture of HIPS-1 and GPPS-1 was processed in the same manner as in Example 6 to prepare specimens to be evaluated for MFR, Izod impact strength, Vicat softening temperature and flame retardance. The results are set forth in Table 6. The specimens thus obtained were each measured for the total content of the remaining styrene monomer and dimerization and trimerization products of styrene in accordance with the measuring method described above. As a result, the foregoing residues were detected in an amount of from 1.1 to 1.5% by weight in all the specimens.

Table 6 shows that the monomeric phosphate having a plurality of aromatic rings substituted by only one alkyl group has a better heat resistance than the monomeric phosphate having only one aromatic ring substituted by only one long-chain alkyl group even if the total number of carbon atoms in the substituents on the aromatic phosphate. It can also be seen that the aromatic phosphate containing hydroxyl group has an excellent heat resistance.

Table 6

	Comparative Examples		Examples		
	28	29	21	22	23
Resin composition					
HIPS-1	70	70	70	70	70
GPPS-1	30	30	30	30	30
Added parts by weight of aromatic phosphate	7	7	7	7	7
Name	Triphenyl phosphate (TPP)	Nonylphenyl-diphenyl phosphate	Octyldecyl-phenyl diphenyl phosphate	Bis(nonylphenyl) phenyl phosphate	Bis(nonylphenyl) resorcinyl phosphate
Total number of carbon atoms in substituents	0	9	18	18	18
Evaluation of molded product					
Flame retardance					
Average flame-out time (sec.)	14	13	14	14	15
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)	20	18	21	16	14
Izod impact strength (kgcm/cm)	8.4	8.4	8.0	8.1	7.8
Vicat softening temperature (°C)	87	89	84	92	95
1 wt% weight loss temperature (°C)	208	231	280	281	278

EXAMPLES 24 TO 33

Monomeric aromatic phosphates obtained under different purification conditions during the purification of FR-1 for the separation of BNPP (set forth in Table 7) were examined for thermal discoloration resistance in accordance with the method described above.

A composition obtained by compounding the aromatic phosphate set forth in Table 7 with 100 parts by weight of a styrene resin comprising 70/30 mixture of HIPS-1 and GPPS-1 was processed in the same manner as in Example 6 to prepare specimens to be evaluated for MFR, Izod impact strength, Vicat softening temperature and flame retardance. The results are set forth in Table 7. The specimens thus obtained were each measured for the total content of the remaining styrene monomer and dimerization and trimerization products of styrene in accordance with the measuring method described above. As a result, the foregoing residues were detected in an amount of from 1.1 to 1.5% by weight in all the specimens.

Table 7 shows that the more the amount of remaining aluminum and nonylphenol as a starting material are, or the higher the acid value is, the more liable to thermal discoloration is the resin composition, and the lower are the flame retardance and heat resistance thereof. It can also be seen that the use of a hindered phenol oxidation inhibitor provides an improvement in thermal discoloration resistance.

Table 7

		Examples									
		24	25	26	27	28	29	30	31	32	33
Resin composition											
HIPS-1		70	70	70	70	70	70	70	70	70	70
GPPS-1		30	30	30	30	30	30	30	30	30	30
Added parts by weight of aromatic phosphate (BNPP)		7	7	7	7	7	7	7	7	7	7
Aluminum content (PPM)		59	58	61	57	60	1.4	723	985	1050	1050
Nonylphenol content (%)		1.5	1.0	0.3	0.3	0.3	0.4	0.4	0.3	0.4	0.4
Acid value (mgKOH/g)		1.0	1.1	1.0	1.5	0.3	0.2	0.2	0.4	0.4	0.4
Antioxidant content (AO) (PPM)		0	0	0	0	0	0	0	0	0	500
Thermal discoloration resistance (% Change)		12000	3000	600	6600	300	200	600	700	5300	500
Evaluation of molded product											
Flame retardance											
Average flame-out tiem (sec.)		12	12	12	13	10	11	13	12	25	25
Dripping of flaiming particles		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement		V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)		16	15	14	15	14	14	15	14	16	16
Izod impact strength (kgcm/cm)		8.1	8.7	8.8	8.6	8.9	8.8	8.7	8.8	7.8	7.8
Vicat softening temperature (°C)		92	94	95	93	96	97	96	96	93	93

<u>EXAMPLES 34 TO 39</u>

A composition obtained by compounding 6 parts by weight of BNPP with 100 parts by weight of HIPS having a reduced viscosity $\eta SP/C$ as set forth in Table 8 was processed in the same manner as in Example 6 to prepare specimens to be evaluated for MFR, Izod impact strength, Vicat softening temperature and flame retardance. The results are set forth in Table 8. The specimens thus obtained were each measured for the total content of the remaining styrene monomer and dimerization and trimerization products of styrene in accordance with the measuring method described above. As a result, the foregoing remaining monomers and oligomers were detected in an amount of from 1.1 to 1.5% by weight in all the specimens.

Table 8 shows that the smaller the reduced viscosity $\eta SP/C$ as an index of the molecular weight of HIPS is, the better is the dripping flame retardance. In particular, when $\eta SP/C$ is from 0.4 to 0.6, the balance of melt flowability impact strength and flame retardance is excellent.

Table 8

		Examples					
		34	35	36#	37#	38#	39
Resin composition							
ηSP/C							
HIPS-2	0.79	100					
HIPS-3	0.60		100				
HIPS-4	0.58			100			
HIPS-1	0.53				100		
HIPS-5	0.40					100	
HIPS-6	0.35						100
BNPP		6	6	6	6	6	6
Evaluation of molded product							
Flame retardance							
Average flame-out tiem (sec.)		25	23	18	15	12	10
Dripping of flaming particles		Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement		V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/min)		10	11	12	13	14	17
Izod impact strength (kgcm/cm)		13	11	10	9	8	5
Vicat softening temperature (°C)		95	95	95	95	94	94

EXAMPLES 40 TO 50

A composition obtained by compounding 7 parts by weight of BNPP with 100 parts by weight of a styrene resin comprising a 70/30 mixture of HIPS-1/GPPS or rubber-unmodified copolymer styrene resin set forth in Table 9 was processed in the same manner as in Example 6 to prepare specimens to be evaluated for MFR, Izod impact strength, Vicat softening temperature and flame retardance. The results are set forth in Table 9. The specimens thus obtained were each measured for the total content of the remaining styrene monomer and dimerization and trimerization products of styrene in accordance with the measuring method described above. As a result, the foregoing remaining monomers and oligomers were detected in an amount of from 1.1 to 1.5% by weight in all the specimens.

Table 9 shows that GPPS having a low molecular weight exhibits a better dripping flame retardance than the others. In particular, the use of GPPS having a weight-average molecular weight of from 130,000 to 220,000 provides an excellent balance of melt flowability, impact strength and flame retardance. Further, the styrene resin obtained by the copolymerization of methacrylic acid or maleic anhydride exhibits an excellent heat resistance. Moreover, styrene resin copolymerized with α-methylstyrene or butyl acrylate are excellent in dripping flame retardance.

In Table 9, Example 40 is the same as Example 22,
which is cited for reference.

Table 9

Properties		Example											
		40	41	42	43	44	45	46	47	48	49	50
Resin composition												
HIPS-1		70	70	70	70	70	70	70	70	70	70	70
Weight-average molecular weight												
GPPS-1	212,000	30										
GPPS-2	160,000		30									
GPPS-3	135,000			30								
GPPS-4	101,000				30							
Methacrylic acid content												
SMAA-1	8%					30						
SMAA-2	7%						30					
SMAA-3	4%							30				
Maleic anhydride content												
SMA-1	8%								30			
SMA-2	15%									30		
α-Methylstyrene content												
SMS	4%										30	
Butyl acrylate content												
SBA	4%											30
BNPP		7	7	7	7	7	7	7	7	7	7	7
Evaluation of molded product												
Flame retardance												
Average flame-out tiem (sec.)		14	13	12	11	25	22	20	24	25	10	10
Dripping of flaming particles		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement		V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/min)		16	17	19	21	9	15	16	9	8	16	25
Izod impact strength (kgcm/cm)		8	8	7	5	9	8	9	10	9	9	10
Vicat softening temperature (°C)		92	92	92	92	96	95	94	95	97	93	88

EXAMPLES 51 TO 60

HIPS-1, GPPS-1, PPE set forth in Table 10, and BNPP were mixed in a weight proportion of 65/35/(amount set forth in Table 10)/7. The mixture was then melt-extruded through a side-feedable twin-screw extruder (ZSK-40mmϕ, available from Werner Pfleiderer Corp.). In some detail, PPE/GPPS mixture was melted at a temperature of 320°C in the stage preceding the extruder. The rest of the resin component and BNPP were side-fed in the stage succeeding the extruder where the mixture was then melt-kneaded at a temperature of 240°C, 295 rpm and an output of 80 kg/hr.

The pellets thus obtained were then processed by an injection molding machine (Type IS80A, available from Toshiba Machine Co., Ltd.) at a cylinder temperature of 230°C and a mold temperature of 60°C to prepare specimens to be evaluated for MFR, Izod impact strength, dart impact strength, flexural strength, flexural modulus, Vicat softening temperature, heat distortion temperature and flame retardance. The results are set forth in Table 10 and Fig. 5. The specimens thus obtained were each measured for the total content of the remaining styrene monomer and dimerization and trimerization products of styrene in accordance with the measuring method described above. As a result, the foregoing remaining monomers and oligomers were detected in an amount of from 1.1 to 1.5% by weight in all the specimens.

Table 10

Properties	Examples									
	51	52	53	54	55	56	57	58	59	60
Resin composition										
HIPS-1	65	65	65	65	65	65	65	65	65	65
GPPS-1	35	35	35	35	35	35	35	35	35	35
Polyphenylene ether (part by weight)	0	1	7	9	13	15	7	7	7	7
Reduced viscosity (ηSP/C)		0.41	0.41	0.41	0.41	0.41	0.25	0.30	0.60	0.65
BNPP	7	7	7	7	7	7	7	7	7	7
Evaluation of molded product										
Flame retardance										
Average flame-out time (sec.)	13.3	13.4	15.2	16.5	20.1	23.8	11.9	13.1	18.9	23.1
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/min)	16.6	15.0	8.4	8.0	4.5	4.0	15.1	12.1	7.8	5.0
Izod impact strength (kgcm/cm)	7.2	7.2	7.1	7.1	7.1	7.2	4.1	6.1	8.3	9.1
Dart impact strength (kgcm)	38.9	39.0	39.1	45.8	47.1	48.5	19.9	29.0	43.1	50.0
Flexural strength (kg/cm^2)	400	420	470	510	540	560	370	440	480	490
Flexural modulus (kg/cm^2)	25300	25400	25500	25700	25900	26000	24500	25000	26000	26500
Vicat softening temperature (°C)	92	94	98	101	105	106	97	98	98	99
Heat distortion temperature (°C)	72	75	78	79	81	82	77	78	78	79

Table 10 and Fig. 5 show that the presence of PPE

provides an improved balance between heat resistance and

rigidity. In particular, when PPE is incorporated in a

rubber-modified styrene resin in an amount of from 3 to 8

5   parts by weight to provide a reduced viscosity ηSP/C of from

0.3 to 0.6, the balance of melt flowability, heat resistance,

rigidity, impact strength and flame retardance can be

remarkably improved.

                        EXAMPLES 61 TO 65

10   The rubber-modified styrene resin comprising HIPS-1

and HIPS-7 in a proportion set forth in Table 11, GPPS-1,

PPE-1 and BNPP were mixed in a weight proportion of

60/40/7/7. The mixture was then examined and evaluated in

the same manner as in Example 51. The results are set forth

15   in Table 11 and Fig. 6. The specimens thus obtained were

each measured for the total content of the remaining styrene

monomer and dimerization and trimerization products of

styrene in accordance with the measuring method described

above. As a result, the foregoing remaining monomers and

20   oligomers were detected in an amount of from 1.1 to 1.5% by

weight in all the specimens.

Table 11

Properties	Examples				
	61	62#	63#	64	65
Resin composition					
HIPS-1 (large size particulate rubber)	60	45	30	15	0
HIPS-7 (small size particulate rubber)	0	15	30	45	60
GPPS-1	40	40	40	40	40
PPE-1	7	7	7	7	7
BNPP	7	7	7	7	7
Evaluation of molded product					
Flame retardance					
Average flame-out time (sec.)	15	16	15	16	17
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)	8.5	8.4	8.4	8.4	8.3
Izod impact strength (kgcm/cm)	6.7	7.1	7.4	6.3	5.1
Dart impact strength (kgcm)	29.0	31.0	33.0	21.0	10.0
Flexural strength (kg/cm^2)	485	510	540	580	620
Flexural modulus (kg/cm^2)	26600	27400	28100	28500	29000
Vicat softening temperature (°C)	99	99	98	98	98
Gloss (%)	41	54	66	78	90

Table 11 and Fig. 6 show that the use of HIPS comprising a large size particulate rubber and a small size particulate rubber provides a remarkable improvement in the balance of external appearance (gloss), rigidity and impact

5   strength.

<div align="center">EXAMPLES 66 TO 68</div>

HIPS-1, GPPS set forth in Table 12, PPE-1 and BNPP were mixed in a weight proportion of 60/40/6/6. The mixture was then examined and evaluated in the same manner as in

10   Example 51. The results are set forth in Table 12 and Fig. 7. The specimens thus obtained were each measured for the total content of the remaining styrene monomer and dimerization and trimerization products of styrene in accordance with the measuring method described above. As a

15   result, the foregoing remaining monomers and oligomers were detected in an amount of from 1.1 to 1.5% by weight in all the specimens.

Table 12

Properties	Examples		
	66	67#	68
Resin composition			
HIPS-1	60	60	60
GPPS-1 Weight-average molecular weight 212,000	40	20	0
GPPS-2 Weight-average molecular weight 160,000	0	20	40
PPE-1	6	6	6
BNPP	6	6	6
Evaluation of molded product			
Flame retardance			
Average flame-out time (sec.)	18	16	14
Dripping of flaming particles	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2
MFR (g/10 min)	8.3	9.8	11.5
Izod impact strength (kgcm/cm)	7.0	6.7	6.3
Dart impact strength (kgcm)	27.0	32.0	34.0
Flexural strength (kg/cm^2)	485	480	475
Flexural modulus (kg/cm^2)	27200	27600	26600
Vicat softening temperature (°C)	99	99	99

Table 12 and Fig. 7 show that the combination of
GPPS's having a high molecular weight and a low molecular
weight provides a remarkable improvement in the balance of
melt flowability, rigidity and impact strength.

5   EXAMPLES 69 TO 85 AND
                     COMPARATIVE EXAMPLES 30 TO 34

HIPS-1, GPPS-1, PPE-1, NDPP set forth in Tables 13-1
and 13-2, BNPP and TNPP were mixed in a weight proportion of
70/30/7. The mixture was then examined and evaluated in the
10   same manner as in Example 51. The results are set forth in
Tables 13-1 and 13-2 and Fig. 8. The specimens thus obtained
were each measured for the total content of the remaining
styrene monomer and dimerization and trimerization products
of styrene in accordance with the measuring method described
15   above. As a result, the foregoing remaining monomers and
oligomers were detected in an amount of from 1.1 to 1.5% by
weight in all the specimens.

Tables 13-1 and 13-2 and Fig. 8 show that if the
total number of carbon atoms in the substituents is from 12
20   to 25 on the number average, i.e., if NPDP content is from 1
to 80% by weight, BNPP content is from 1 to 98% by weight,
and TNPP content is from 1 to 98% by weight, the balance of
flame retardance, non-volatility, melt flowability, impact
resistance, impact strength, water-resistant gloss retention,
25   and surface hardness of molded product thus obtained is
excellent. In particular, as compared with a simple average

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of NDPP and TNPP, the mixture of the foregoing three kinds of
monomeric phosphates provides improvements in water-resistant
gloss retention and Vicat softening temperature (the curve
bends upward in Fig. 8). A mixture of monomeric aromatic
5   phosphates substituted by different numbers of nonyl groups
can exert a unique effect.

Table 13-1

Properties	Comparative Examples					Examples						
	30	31	32	33	34	69	70	71	72	73	74	75
Resin composition												
HIPS-1	70	70	70	70	70	70	70	70	70	70	70	70
GPPS-1	30	30	30	30	30	30	30	30	30	30	30	30
Add parts by weight of aromatic phosphate	7	7	7	7	7	7	7	7	7	7	7	7
Total number of carbon atoms in substituents on the number average	9	27	9.9	26.1	25.2	18	12.2	15.3	18.0	20.7	24.3	24.6
Nonyl phenyl diphenyl phosphate (NDPP) Total number of carbon atoms in substituents: 9	100	0	90	0	10	0	80	60	45	30	10	1
Bis(nonylphenyl)phenyl phosphate (BNPP) Total number of carbon atoms in substituents: 18	0	100	10	10	0	100	5	10	10	10	10	20
Tris(nonylphenyl) phosphate (TNPP) Total number of carbon atoms in substituents: 27	0	100	0	90	90	0	15	30	45	60	80	74
Evaluation of molded product												
Flame retardance												
Average flame-out time (sec.)	13	28	16	27	26	14	13	14	14	14	16	15
Dripping of flaiming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	yes	Yes	Yes	Yes
UL-94 judgement	V-2	HB*	V-2	HB*	HB*	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)	18.3	13.0	17.5	13.8	14.0	16.0	17.2	16.6	16.1	16.0	15.9	15.8
Izod impact strength (kgcm/cm)	8.4	7.9	8.4	7.9	7.9	8.1	8.3	8.2	8.1	8.1	8.0	8.0
Vicat softening temperature (°C)	89.0	94.0	89.5	94.1	94.0	92.3	90.4	91.4	92.2	93.9	94.0	94.1
Water-resistant gloss retention (ΔG) (%)	55	21	49	21	21	25	40	31	25	23	21	21
Pencil hardness	3B	B	3B	B	B	2B	2B	2B	2B	B	B	B
Residual amount after 5 minutes of 250°C storage (TGA method) (%)	75	97	82	97	97	96	95	96	96	97	97	97

Table 13-2

Properties	Examples									
	76	77	78	79	80	81	82	83	84	85
Resin composition										
HIPS-1	70	70	70	70	70	70	70	70	70	70
GPPS-1	30	30	30	30	30	30	30	30	30	30
Add parts by weight of aromatic phosphate	7	7	7	7	7	7	7	7	7	7
Total number of carbon atoms in substituents on the number average	22.3	20.7	18.9	18.0	17.1	15.3	18.0	16.4	22.5	18.1
Nonyl phenyl diphenyl phosphate (NDPP) Total number of carbon atoms in substituents: 9	1	10	20	25	30	40	10	19	10	2
Bis(nonylphenyl)phenyl phosphate (BNPP) Total number of carbon atoms in substituents: 18	50	50	50	50	50	50	80	80	30	95
Tris(nonylphenyl) phosphate (TNPP) Total number of carbon atoms in substituents: 27	49	40	30	25	20	10	10	1	60	3
Evaluation of molded product										
Flame retardance										
Average flame-out time (sec.)	15	13	14	14	13	14	14	14	16	14
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)	16.0	16.0	16.1	15.9	16.2	16.5	16.1	16.4	16.0	16.0
Izod impact strength (kgcm/cm)	8.1	8.1	8.1	8.0	8.2	8.3	8.0	8.2	8.0	8.0
Vicat softening temperature (°C)	93.8	93.8	92.8	92.2	91.9	91.2	92.1	91.8	93.9	92.3
Water-resistant gloss retention (ΔG) (%)	22	23	24	25	26	31	25	28	22	25
Pencil hardness	B	B	2B	2B	2B	2B	2B	2B	B	2B
Residual amount after 5 minutes of 250°C storage (TGA method) (%)	97	97	96	96	96	96	96	96	97	96

EXAMPLES 86 TO 103

HIPS set forth in Table 14 and an monomeric aromatic

phosphate comprising NPDP, BNPP and TNPP in a weight

proportion of 10/50/40, or HIPS-1, GPPS-1, and PPE set forth

5   in Table 15, and the foregoing monomeric aromatic phosphate

were mixed in a weight proportion set forth in Tables 14 and

15. The mixtures were each then examined and evaluated in

the same manner as in Example 51. The results are set forth

in Tables 14 and 15. The specimens thus obtained were each

10   measured for the total content of the remaining styrene

monomer and dimerization and trimerization products of

styrene in accordance with the measuring method described

above. As a result, the foregoing remaining monomers and

oligomers were detected in an amount of from 1.1 to 1.5% by

15   weight in all the specimens.

Tables 14 and 15 show that if ηSP/C of HIPS is from

0.4 to 0.6, the balance of melt flowability, impact strength

and flame retardance is excellent and the presence of PPE

further provides an improved balance between heat resistance

20   and rigidity. In particular, when PPE is incorporated in a

rubber-modified styrene resin in an amount of from 3 to 8

parts by weight to provide a reduced viscosity ηSP/C of from

0.3 to 0.6, the balance of melt flowability, heat resistance,

rigidity, impact strength and flame retardance can be

25   remarkably improved. Further, HIPS copolymerized with

α-methylstyrene or butyl acrylate is excellent in dripping

flame retardance.

Table 14

Properties	Examples							
	86	87	88#	89#	90#	91	92	93
Resin composition								
ηSP/C								
HIPS-2 0.79	100							
HIPS-3 0.60		100						
HIPS-4 0.58			100					
HIPS-1 0.53				100				
HIPS-5 0.40					100			
HIPS-6 0.35						100		
MS-HIPS 0.53							100	
BA-HIPS 0.53								100
Aromatic phosphate (NDPP/BNPP/TNPP=10/50/40)	6	6	6	6	6	6	6	6
Evaluation of molded product								
Flame retardance								
Average flame-out time (sec.)	19	17	12	9	8	7	6	6
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/min)	10	11	12	13	14	17	12	18
Izod impact strength (kgcm/cm)	14	12	11	10	9	6	9	11
Vicat softening temperature (°C)	97	97	97	97	96	96	98	93

Table 15

Properties	Examples									
	94	95	96	97	98	99	100	101	102	103
Resin composition										
HIPS-1	65	65	65	65	65	65	65	65	65	65
GPPS-1	35	35	35	35	35	35	35	35	35	35
Polyphenylene ether (part by weight)	0	1	7	9	13	15	7	7	7	7
Reduced viscosity (ηSP/C)		0.41	0.41	0.41	0.41	0.41	0.25	0.30	0.60	0.65
Aromatic phosphate (NDPP/BNPP/TNPP=10/50/40)	7	7	7	7	7	7	7	7	7	7
Evaluation of molded product										
Flame retardance										
Average flame-out time (sec.)	13	13	15	16	17	19	13	15	20	24
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)	16.5	15.1	8.3	8.1	4.6	4.2	15.0	12.3	7.9	5.0
Izod impact strength (kgcm/cm)	8.0	8.0	8.1	8.1	7.9	6.1	5.1	7.1	9.3	10.1
Dart impact strength (kgcm)	38.1	40.0	39.1	45.8	48.1	49.5	20.9	30.0	43.1	50.0
Flexural strength (kg/cm^2)	440	460	510	550	580	600	370	480	520	530
Flexural modulus (kg/cm^2)	25800	25900	26000	26300	26400	26500	24600	25500	26500	27000
Vicat softening temperature (°C)	94	98	101	104	108	110	100	101	101	102
Heat distortion temperature (°C)	74	78	81	82	84	85	80	81	81	82

EXAMPLES 104 TO 112

Compositions obtained by compounding HIPS-1, GPPS-1,
PPE-1, a polydimethylsiloxane (silicone) set forth in Table
16, and BNPP in a weight proportion of 70/30/(0 or 7)/(amount
5   set forth in Table 16) were each then examined and evaluated
in the same manner as in Example 51. The results are set
forth in Table 16. The specimens thus obtained were each
measured for the total content of the remaining styrene
monomer and dimerization and trimerization products of
10   styrene in accordance with the measuring method described
above. As a result, the foregoing remaining monomers and
oligomers were detected in an amount of from 1.1 to 1.5% by
weight in all the specimens.

Table 16 gives a presumption that the use of silicone
15   reduces the heat shrinkage of molded product, resulting in a
rise in the ease of melting and dripping upon ignition and
hence an improvement in flame retardance. This fact suggests
that the incorporation of silicone relaxes the orientation of
the molded product.

Table 16

		Examples							
Properties	104	105	106#	107#	108	109	110	111	112#
Resin composition									
HIPS-1	70	70	70	70	70	70	70	60	60
GPPS-1	30	30	30	30	30	30	30	40	40
PPE-1	0	0	0	0	0	0	0	7	7
BNPP	7	7	7	7	7	7	7	7	7
Polydimethyl siloxane	0	2	2	2	2	2	2	0	1
(kinematic viscosity CS)	-	20	50	100	1000	20000	25000	-	50
% Volatility loss (150°C, 24 hr.)	-	5	≤0.5	≤0.5	≤0.5	≤0.5	≤0.5	-	≤0.5
Evaluation of molded product									
Flame retardance									
Average flame-out time (sec.)	16.0	9.9	10.4	22.9	22.0	23.1	25.0	15.3	13.2
Dripping of flaiming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
% Heat shrinkage	29	26	26	27	28	28	29	32	27

EXAMPLES 113 TO 118

Resin compositions comprising styrene resins and
other thermoplastic resins having the formulations set forth
in Table 17 were prepared and evaluated in the same manner as
5   in Example 51. The results are set forth in Table 17.

Table 17

Properties	Examples					
	113	114	115	116	117	118
Resin composition						
HIPS-1	100	100	100			
ABS						100
PPE-1	100	100	50	100	100	
PC						500
BNPP	20	20	25	100	500	
Oligomeric aromatic phosphate (fr-1)		10		20	10	10
Evaluation of molded product						
Flame retardance						
Average flame-out time (sec.)	5.0	2.1	4.5	4.8	2.1	1.9
Dripping of flaming particles	None	None	None	None	None	None
UL-94 judgement	V-0	V-0	V-0	V-0	V-0	V-0

EXAMPLES 119 TO 124 AND
COMPARATIVE EXAMPLE 35

Compositions obtained by compounding PPE, UVA, HALS

and TiO$_2$ with BNPP in a weight proportion set forth in Table

5   18 per 100 parts by weight of a styrene resin comprising

HIPS-1 and GPPS-1 in a weight proportion of 60/40 were each

processed in the same manner as in Example 51 to prepare

specimens which were then evaluated in accordance with the

light resistance testing method described above. For

10   comparison, a flame retardant polystyrene flame-retarded by a

halogen flame retardant (BEO) was evaluated. The results are

set forth in Table 18.

Table 18 shows that the flame retardant polystyrene

comprising the flame retardant of the present invention

15   exhibits an excellent light resistance as compared with the

halogen flame retardant polystyrene.

Table 18

Example No.	Examples						Comparative Example 35
	119	120	121	122	123	124	
Resin composition							
HIPS-1	60	60	60	60	60	60	60
GPPS-1	40	40	40	40	40	40	40
PPE-1	0	0	7	7	10	10	0
BNPP	7	7	7	7	7	7	0
BEO	0	0	0	0	0	0	5
SB$_2$O$_3$	0	0	0	0	0	0	1
Ultraviolet light absorber (UVA)	0	0.3	0	0.3	0	0.3	0.3
Light stabilizer (HALS)	0	0.1	0	0.1	0	0.1	0.1
Sunproofing agent (TiO$_2$)	1	1	1	1	1	1	1
Light resistance [color difference ΔE (300 hr.)]	5.3	0.6	6.6	2.8	7.2	2.7	10.5

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EXAMPLES 125 TO 132 AND
COMPARATIVE EXAMPLES 36 TO 43

Rubber-modified polystyrenes having different

contents of remaining styrene monomers and oligomers were

5   prepared by altering the polymerization temperature and

amount of chain transfer agent to prepare polystyrenes having

a large content of remaining styrene monomers and oligomers

(dimerization and trimerization products of styrene), and

then compounding these polystyrenes with HIPS obtained by the

10   purification of HIPS-1. Compositions obtained by compounding

7 parts by weight of tris(nonylphenyl)phosphate (TNPP),

tris(diisopropylphenyl) phosphate (TDIP), tris(phenylphenyl)

phosphate (TPPP) or bis(nonylphenyl)phenylphosphate (BNPP)

with 100 parts by weight of a styrene resin obtained by

15   mixing the rubber-modified styrene resin and GPPS-1 in a

proportion of 70/30 were each processed in the same manner as

in Example 51 to prepare specimens which were then evaluated

for flame retardance. The results are set forth in Table 19

and Fig. 9.

20   Table 19 and Fig. 9 show that flame retardants having

a volatility loss of not less than 50% by weight at 400°C

such as BNPP exhibit an excellent flame retardance and thus

do not show great a dependence of flame retardance on the

content of remaining styrene monomers and oligomers.

25   However, among the flame retardants, the aromatic phosphate

having a low volatility at 400°C has a great dependence of

flame retardance on the remaining monomers and ologomers. Thus, when the content of the foregoing residue is not more than 1% by weight, the flame retardance of the resin composition can be drastically enhanced.

Table 19

Properties	Ex. 125	Ex. 126	Comp. Ex. 36	Comp. Ex. 37	Ex. 127	Ex. 128	Comp. Ex. 38	Comp. Ex. 39	Ex. 129	Ex. 130	Comp. Ex. 40	Comp. Ex. 41	Ex. 131	Ex. 132	Comp. Ex. 42	Comp. Ex. 43
Resin composition																
HIPS-1	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
GPPS-1	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Monomeric aromatic phosphate																
Name	Tris(nonylphenyl) phosphate				Tris(diisopropylphenyl) phosphate				Tris(phenylphenyl) phosphate				Bis(nonylphenyl) phenyl phosphate			
Total number of carbon atoms in substituents	27	27	27	27	18	18	18	18	18	18	18	18	18	18	18	18
Weight loss (400°C) (TAG)	23	23	23	23	33	33	33	33	25	25	25	25	65	65	65	65
Added wt. parts	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Content of Remaining styrene, oligomer (wt%)	0.1	1.0	1.2	2.0	0.1	1.0	1.2	2.0	0.1	1.0	1.2	2.0	0.1	1.0	1.2	2.0
Evaluation of molded product																
Flame retardance																
Average flame-out time (sec.)	12	16	29	41	10	13	26	29	11	15	28	39	11	12	13	15
Dripping of flaiming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	HB*	HB*	V-2	V-2	HB*	HB*	V-2	V-2	HB*	HB*	V-2	V-2	V-2	V-2

EXAMPLES 133 TO 161 AND
COMPARATIVE EXAMPLES 44 TO 47

HIPS or PPE having different reduced viscosities
$\eta SP/C$ set forth in Tables 20 to 22 and TNPP, TDIP or TPPP as
a monomeric aromatic phosphate were mixed in a percent
composition in such a manner that the total content of
remaining styrene monomer and dimerization and trimerization
products of styrene was 0.5% by weight. The compositions
thus obtained were each then examined and evaluated in the
same manner as in Example 51. The results are set forth in
Tables 20 to 22.

Tables 20 to 22 show that when the total content of
remaining styrene monomer and dimerization and trimerization
products of styrene in the molded product is not more than
1.0% by weight and $\eta SP/C$ of HIPS is from 0.4 to 0.6, the
balance of melt flowability, impact strength and flame
retardance is excellent. Further, the presence of PPE
provides improvements in the balance of heat resistance and
rigidity. In particular, when PPE having a reduced viscosity
$\eta SP/C$ of from 0.3 to 0.6 is incorporated in a rubber-modified
styrene resin in an amount of from 3 to 8 parts by weight,
the balance of melt flowability, heat resistance, rigidity,
impact strength and flame retardance is further enhanced.
When the content of TNPP, TDIP or TPPP is from 3 to 30 parts
by weight, the foregoing properties are drastically enhanced.

Table 20

Properties	Examples							
	133	134	135	136	137	138	139	140
Resin composition								
ηSP/C								
HIPS-2　0.79	100							
HIPS-3　0.60		100						
HIPS-4　0.58			100					
HIPS-1　0.53				100			100	100
HIPS-5　0.40					100			
HIPS-6　0.35						100		
TNPP	6	6	6	6	6	6		
TDIP							6	
TPPP								6
Z Content of remaining styrene monomer, oligomer	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Evaluation of molded product								
Flame retardance								
Average flame-out time (sec.)	22	20	18	16	9	8	14	16
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/min)	9	10	11	12	13	16	13	10
Izod impact strength (kgcm/cm)	13	11	10	9	8	5	8	8
Vicat softening temperature (°C)	96	96	96	96	95	95	95	97

Table 21

Properties	Examples											
	141	142	143I	144I	145	146	147	148	149	150	151I	152I
Resin composition												
HIPS-1	65	65	65	65	65	65	65	65	65	65	65	65
GPPS-1	35	35	35	35	35	35	35	35	35	35	35	35
Polyphenylene ether (weight parts)	0	1	7	9	13	15	7	7	7	7	7	7
Reduced viscosity (ηP/C)	0.41	0.41	0.41	0.41	0.41	0.41	0.25	0.30	0.60	0.65	0.60	0.65
TNPP	7	7	7	7	7	7	7	7	7	7	0	0
TDIP	0	0	0	0	0	0	0	0	0	0	7	0
TPPP	0	0	0	0	0	0	0	0	0	0	0	7
Content of remaining styrene, oligomer (wt%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Evaluation of molded product												
Flame retardance												
Average flame-out time (sec.)	14	14	15	17	18	20	14	16	21	25	14	16
Dripping of flaiming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)	14.6	13.0	7.1	6.0	5.0	4.2	13.1	10.1	5.8	4.0	8.1	5.1
Izod impact strength (kg·cm/cm)	7.0	7.0	7.1	7.1	6.9	7.1	4.1	6.1	8.3	9.1	8.1	6.1
Dart impact strength (kg·cm)	36.1	37.0	37.1	43.8	45.1	46.5	17.9	27.0	41.1	48.0	39.1	35.1
Flexural strength (kg/cm²)	420	440	490	530	560	580	350	460	500	510	470	510
Flexural modulus (kg/cm²)	25500	25600	25700	25900	26100	26200	24200	25200	26200	26700	25300	26000
Vicat softening temperature (°C)	94	97	100	103	107	109	99	100	100	101	99	101
Heat distortion temperature (°C)	74	77	80	81	83	84	79	80	80	81	79	81

Table 22

Properties	Comp. Ex. 44	Examples 153	154	155	156	157	158	159	160	161	Comp. Ex. 45	46	47
Resin composition													
HIPS-1	60	60	60	60	60	60	60	60	60	60	60	60	60
GPPS-1	40	40	40	40	40	40	40	40	40	40	40	40	40
PPE-1	7	7	7	7	7	7	7	7	7	7	7	7	7
TNPP	0	3	0	0	8	0	0	30	0	0	32	0	0
TDIP	0	0	3	0	0	8	0	0	30	0	0	32	0
TPPP	0	0	0	3	0	0	8	0	0	30	0	0	32
Wt% Content of remaining styrene monomer, oligomer	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Evaluation of molded product													
Flame retardance													
Average flame-out time (sec.)	60	25	24	21	16	14	15	9	8	7	8	7	7
Dripping of flaming particles	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
UL-94 judgement	HB*	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2	V-2
MFR (g/10 min)	3	6	6	4	7	8	5	15	17	11	18	19	11
Izod impact strength (kgcm/cm)	9	8	9	7	7	8	6	6	7	6	5	5	5
Vicat softening temperature (°C)	103	101	100	102	99	98	100	94	93	95	86	85	87

EXAMPLE 162 AND
COMPARATIVE EXAMPLES 48 TO 53

Resin compositions comprising HIPS-1, GPPS, PPE-1 and BNPP in a weight proportion of 60/40/7/7 were prepared. In detail, the mixture was melt-kneaded at 295 rpm and an output rate of 80 kg/hr by means of a side-feedable twin-screw extruder (ZSK-40mmφ, available from Werner Pfleiderer Corp.) under the conditions set forth in Table 23 to prepare various resin compositions.

The resin compositions thus obtained were each then processed through an injection molding machine (resin temperature: 230°C) to prepare specimens which were then evaluated for flame retardance and external appearance. The results are set forth in Table 23.

Table 23

Example No.	Method of adding resin component and polymer additive	Extruder cylinder temperature (°C) Pre-stage	Post-stage	% Polyphenylene content in pre-stage resin	Flame retardance UL-94	Tensile elongation (%)	Extrusion condition	External appearance
Comparative Example 48	Simultaneous addition	300		-	V-2	8	Unmolten matter in polymer strand	Unmolten matter
Example 162	Separative addition (resin component and polymer additive separated)	320	220	55	V-2	25	Good	No unmolten matter
Comparative Example 49	"	320	180	55	HB*	25	Organic phosphorus blown out from die	No unmolten matter
Comparative Example 50	"	240	240	55	V-2	6	Unmolten matter in polymer strand	Unmolten matter
Comparative Example 51	"	320	320	55	HB*	3	Good	No unmolten matter
Comparative Example 52	"	320	220	40	V-2	7	Unmolten matter in polymer strand	Unmolten matter
Comparative Example 53	"	370	220	55	V-2	3	Good	No unmolten matter

The following facts can be seen in Table 23.

If the mixture is melt-kneaded without separating the resin component from the polymer additive, unmolten polyphenylene ether is produced, causing a remarkable drop in external appearance and particularly in tensile elongation.

Further, if the polyphenylene ether content of the resin component to be fed in the stage preceding the extruder falls below 50% by weight, no shearing force can be applied, causing the production of unmolten matters.

EXAMPLES 163 TO 170 AND COMPARATIVE EXAMPLES 54 TO 57

The following resin compositions were each mechanically mixed, and then melt-kneaded through a side-feedable twin-screw extruder (ZSK, available from Werner Pfleiderer Corp.; cylinder inner diameter D = 40 mm or 70 mm) (see Fig. 10).

For the preparation of master batches (MB-1, MB-2), the resin component was fed through a main feeder in the stage preceding the extruder (above the side feed opening) where it was melted at a barrel temperature of 320°C. Subsequently, BNPP was fed through side feeders in the stage succeeding the extruder (below the side feed opening) where it was melt-kneaded with the foregoing mixture at a barrel temperature of 270°C. (Number of revolutions: 295 rpm; output: 80 kg/hr)

MB-1: PPE-1/BNPP = 65/35

MB-2: PPE-1/GPPS-1/BNPP = 40/40/20

Final compositions comprising HIPS-1, GPPS-1, PPE-1
and BNPP in a proportion of 60/40/7/7 were prepared in the
following manners (feed process I, II or III):

I (MB-1 was used): HIPS-1/GPPS-1/MB-1/BNPP

MB-1 and the remaining components other than BNPP
were fed through the main feeder in the stage exceeding the
extruder where they were melted at a barrel temperature of
270°C. Subsequently, BNPP was fed through the side feeders
in the stage succeeding the extruder where it was melt-
kneaded with the foregoing mixture at a barrel temperature of
270°C. (Number of revolutions: 295 rpm; output: 80 kg/hr)

II (MB-2 was used): HIPS-1/GPPS-1/MB-2

All the components were fed through the main feeder,
and then melt-kneaded at a barrel temperature of 270°C.
(Number of revolutions: 295 rpm; output: 80 kg/hr)

III (no master batches were used): HIPS-1/GPPS-1/PPE-1/BNPP

PPE-1 and GPPS-1 were extruded in a weight proportion
of 7/5 in the stage preceding the extruder under the same
conditions as the foregoing master batches. Subsequently, in
the stage succeeding the extruder the remaining resin
components and components other than BNPP were fed through
one side feeder while BNPP was fed through another side

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feeder so that they were extruded under the same conditions
as the foregoing composition.

The pellets thus obtained were then processed at a
cylinder temperature of 230°C and a mold temperature of 60°C
by means of the same injection molding machine as described
in Example 51 to prepare specimens which were then evaluated
for various physical properties. The results are set forth
in Table 24.

Table 24

Example No.	L/D	Extruder size (apparatus constant)				Feed process	Extrusion condition
		Length L₁ of kneading zone between main feed and side feed openings	Length L₂ of kneading zone between tip and side feed opening	Total Length L₁+L₂ of kneading zone of extruder	Length L₃ of space between main feed and side feed openings		
Example 163	46	8.9D	3.6D	12.5D	32.9D	I	Good
Example 164	46	8.9D	3.6D	12.5D	32.9D	II	Good
Example 165	38	6.6D	4.9D	11.5D	22.4D	I	Good
Comparative Example 54	38	0	11.5D	11.5D	22.4D	I	Unmolten matter of PPE, bentup
Comparative Example 55	38	11.5D	0	11.5D	22.4D	I	Bentup
Comparative Example 56	38	D	10.5D	11.5D	22.4D	I	Unmolten matter of PPE
Comparative Example 57	38	10.5D	D	11.5D	22.4D	I	Bentup
Example 166	46	6.6D	4.9D	11.5D	32.9D	I	Good
Example 167	46	8.9D	3.6D	12.5D	32.9D	I	Good
Example 168	30	4.4D	6.4D	10.8D	12.4D	I	Good
Example 169	46	8.9D	3.6D	12.5D	32.9D	II	Good
Example 170	46	8.9D	3.6D	12.5D	32.9D	III	Good

EXAMPLES 171 TO 176 AND
COMPARATIVE EXAMPLES 58 TO 65

For the preparation of resin compositions comprising

HIPS-1, GPPS-1, PPE-1 and BNPP in a proportion of 60/40/7/7,

5   the master batches set forth in Table 25 were each melt-

kneaded through a side-feedable twin-screw extruder,

subsequently followed by melt kneading in the following feed

processes (A, B and C processes).

In the first stage extrusion (preparation of master

10   batch), the resin components were fed through the main

feeder, and then melted at a barrel temperature of 320°C.

Subsequently, BNPP was fed through the side feeders, and then

melt-kneaded with the foregoing resin components at a barrel

temperature of 270°C. Subsequently, in the second stage

15   extrusion, the material was melt-kneaded at a barrel

temperature of 270°C in the feed processes A, B and C. (See

Table 26) The extrusion conditions in these feed processes

comprise 295 rpm and output of 80 kg/hr. at both the first

and second stages.

Table 25

No.	Glass transition temperature (°C)	Master batch formulation			
		Resin			Phosphate
		PPE-1	HIPS-1	GPPS-1	BNPP
MB-3	65	60			40
MB-4	80	65			35
MB-5	94	41	30	10	19
MB-6	104	67	8	8	17
MB-7	172	70		30	
PPE-1	226	100			

The pellets thus obtained were each processed at a
cylinder temperature of 230°C and a mold temperature of 60°C
by means of the same injection molding machine as described
in Example 45 to prepare specimens which were then evaluated
5   for various physical properties.   The results are set forth
in Table 26 and Fig. 12.

Table 26

Example	1st stage extrusion Master batch No.	Glass transition temp. (°C)	Feed process	Cylinder dia. D (mm)	Extruder output Q (kg/h)	Number of revolutions N (rpm)	Kneadability* (×10⁻⁷)	2nd stage extrusion Dart impact strength (kgcm)	External appearance	Extrusion stability
Example 171	MB-3	94	A	37	51	500	6.41	39	Good	Good
Example 172	MB-3	94	A	73	227	270	6.88	40	Good	Good
Example 173	MB-3	94	A	40	80	295	13.49	38	Good	Good
Example 174	MB-3	94	A	40	60	295	10.12	39	Good	Good
Example 175	MB-2	80	A	40	80	295	13.49	35	Good	Good
Comparative Example 58	MB-4	104	A	40	80	295	13.49	18	Unmolten matter	Good
Comparative Example 59	MB-4	104	A	40	60	295	10.12	21	Good	Good
Comparative Example 60	MB-4	104	A	73	216	220	8.03	25	Good	Good
Comparative Example 61	MB-5	172	A	40	80	295	13.49	5	Unmolten matter	Good
Comparative Example 62	MB-1	65	A	40	80	295	13.49	Hopper blocked by resin		
Example 176	MB-3	94	B	40	80	295	13.49	40	Good	Good
Comparative Example 63	MB-4	104	B	40	80	295	13.49	28	Good	Good
Comparative Example 64	-	-	C	40	80	295	13.49	17	Unmolten matter	Instable
Comparative Example 65	-	-	A	40	80	295	13.49	5	Unmolten matter	Instable

*: Kneadability parameter = Extrusion factor/circumferential speed of screw = $(Q/D^2)/\pi ND$

<u>Feed process (See Fig. 11)</u>

Process A: Main feed (components other than BNPP)

               Side feed (BNPP)

Process B: Main feed (master batch)

               Side feed (BNPP)

               Side feed (master batch, components other than BNPP)

Process C: Main feed (PPE/GPPS)

               Side feed (BNPP)

               Side feed (PPE/components other than GPPS and BNPP)

Table 26 and Fig. 12 show that when the master batch having a glass transition temperature (Tg) of from 70°C to 100°C obtained by compounding a polyphenylene ether, a monomeric aromatic phosphate (BNPP), and optionally a rubber-modified styrene resin or rubber-unmodified styrene resin is melt-kneaded with the remaining components, a flame retardant resin composition having an excellent dart impact strength can be obtained. It can also be seen that if the glass transition temperature of the master batch exceeds 100°C, the resulting resin composition shows a great dependence of dart impact strength on the kneadability parameter.

The incorporation of the low volatility flame retardant for styrene resin of the present invention in a styrene resin composition can provide a resin composition which causes remarkably little mold deposit even after a

5   prolonged continuous molding and exhibits excellent flame retardance, impact resistance, heat resistance, melt flowability, water-resistance gloss retention, and surface hardness of molded product.

The resin composition comprising the low volatility

10   flame retardant for styrene resin is suitable for housing, shassis or parts of household appliance such as VTR, panel baord, TV, audio player, capacitor, power outlet, radio-tape player/recorder, video tape housing, video disk player, air conditioner, air moistener and electric heater; housing,

15   shassis or parts of OA (office automation) apparatus such as main frame (mechanical shassis) of CDROM, printer, facsimile, PPC, CRT, word processor, copying machine, electronic cash register, office computer system, floppy disk drive, keyboard, typewriter, ECT, calculator, toner cartridge and

20   telephone; electric and electronic parts such as connector, coil bobbin, switch, relay, relay socket, LED, variable condensor, AC adaptor, FBT high-voltage bobbin, FBT case, IFT coil bobbin, jack, volume shaft and motor part; automoble parts such as instrument panel, radiator grill, cluster,

25   speaker grill, louver, console box, defroster garnish,

ornament, fuse box, relay case and connector shift tape; and other various usage.

CLAIMS

1. A low volatility flame retardant for a styrene
resin comprising an aromatic phosphate represented by formula
(I):

5

                                                          (I)

wherein a, b, and c each independently represent an integer
of from 1 to 3; and R_1, R_2, and R_3 each independently
represent a hydrogen atom or a halogen-free alkyl group
having from 1 to 30 carbon atoms, which is not an isopropyl

10   group,

      the total number of carbon atoms in the substituents
represented by R_1, R_2 and R_3 being from 12 to 25 on an average
in one molecule of said aromatic phosphate,

      provided that when said flame retardant comprises a

15   plurality of aromatic phosphates having different
substituents, the total number of carbon atoms in the
substituents R_1, R_2 and R_3 of said flame retardant is

represented by a number average in the whole of said flame
retardant, which is the sum of the products of the weight
fraction of respective aromatic phosphate and the total
number of carbon atoms in the substituents in respective

5   aromatic phosphate.

2.   A flame retardant as claimed in Claim 1, wherein
the total number of carbon atoms in the substituents R_1, R_2
and R_3 is from 14 to 22.

3.   A flame retardant as claimed in Claim 1, wherein

10 the total number of carbon atoms in the substituents R_1, R_2
and R_3 is from 16 to 20.

4.   A flame retardant as claimed in Claim 1, wherein
said flame retardant comprises nonylphenyl diphenylphosphate,
bis(nonylphenyl) phenylphosphate, and tris(nonylphenyl)

15 phosphate.

5.   A flame retardant as claimed in Claim 4, wherein
the total number of carbon atoms in the substituents R_1, R_2
and R_3 is from 16 to 20.

6.   A flame retardant as claimed in any one of Claims

20 1 to 5, wherein the content of aromatic phosphates having a
total number of carbon atoms in the substituents R_1, R_2 and R_3
of less than 12 is not more than 20% by weight.

7.   A flame retardant as claimed in any one of Claims
1 to 6, said flame retardant exhibits an acid value of not

25 more than 1 mgKOH/g as defined in JIS-K6751 and/or said flame

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retardant has an alkylphenol content of not more than 1% by
weight.

8. A flame retardant as claimed in any one of Claims
1 to 7, the total content of aluminum, magnesium, sodium and
antimony in said flame retardant is not more than 1,000 ppm
by weight.

9. A flame retardant as claimed in any one of Claims
1 to 8, said flame retardant further comprises a hindered
phenol anitoxidant in an amount of from 1 to 1,000 ppm by
weight.

10. A flame retardant as claimed in any one of
Claims 1 to 9, said flame retardant is a dripping flame
retardant.

11. A resin composition comprising 100 parts by
weight of a styrene resin and from 1 to 50 parts by weight of
said flame retardant as claimed in any one of Claims 1 to 10.

12. A resin composition as claimed in Claim 11,
wherein said resin composition comprises 100 parts by weight
of a styrene resin and from 1 to 20 parts by weight of said
flame retardant.

13. A resin composition as claimed in Claim 12,
wherein said resin composition comprises 100 parts by weight
of a styrene resin and from 3 to 8 parts by weight of said
flame retardant.

14. A resin composition as claimed in any one of
Claims 11 to 13, wherein said resin composition further

comprises a polyphenylene ether and/or an aromatic polycarbonate in an amount of from 1 to 500 parts by weight per 100 parts by weight of said styrene resin.

15. A resin composition as claimed in any one of Claims 11 to 13, wherein said resin composition further comprises a polyphenylene ether in an amount of from 1 to 40 parts by weight per 100 parts by weight of said styrene resin.

16. A resin composition as claimed in Claim 15, wherein the amount of said polyphenylene ether is from 3 to 8 parts by weight per 100 parts by weight of said styrene resin.

17. A resin composition as claimed in any one of Claims 11 to 16, said resin composition further comprises a polyorganosiloxane in an amount of from 0.01 to 10 parts by weight per 100 parts by weight of said styrene resin.

18. A resin composition as claimed in Claim 17, wherein said polyorganosiloxane is a polydimethylsiloxane.

19. A resin composition as calimed in any one of Claims 11 to 18, wherein the reduced viscosity $\eta SP/C$ of said styrene resin is from 0.4 to 0.6 dl/g.

20. A resin composition as claimed in any one of Claims 14 to 19, said resin composition further comprises a polyphenylene ether having a reduced viscosity $\eta SP/C$ of from 0.3 to 0.6 dl/g.

21. A resin composition as claimed in any one of
Claims 11 to 20, wherein said styrene resin is a rubber-
modified styrene resin comprising a small size particulate
rubber having a weight-average particle diameter of from 0.1

5   to 0.9 µm and a large size particulate rubber having a
weight-average particle diameter of from 1.0 to 3.0 µm.

22. A flame retardant resin composition comprising
100 parts by weight of a styrene resin and from 3 to 30 parts
by weight of a flame retardant selected from the group

10   consisting of:

(1) a flame retardant comprising an aromatic
phosphate represented by formula (I):

(I)

wherein $\underline{a}$, $\underline{b}$, and $\underline{c}$ each independently represent an integer

15   of from 1 to 3; and at least one of by R_1, R_2, and R_3
represent an isopropyl group or an aryl group, the others of
R_1, R_2, and R_3 each independently represent a hydrogen atom or

a halogen-free alkyl group having from 1 to 30 carbon atoms, which is not an isopropyl group,

the total number of carbon atoms in the substituents represented by R_1, R_2 and R_3 being from 12 to 25 on an average in one molecule of said aromatic phosphate,

provided that said flame retardnat comprises a plurality of aromatic phosphates having different substituents, the total number of carbon atoms in the substituents R_1, R_2 and R_3 of said flame retardant is represented by a number average in the whole of said flame retardant, which is the sum of the products of the weight fraction of respective aromatic phosphate and the total number of carbon atoms in the substituents in respective aromatic phosphate, and

(2) tris(nonylphenyl) phosphate,

wherein the total content of aromatic vinyl monomers and dimerization and trimerization products of aromatic vinyl monomers remaining in said resin composition is not more than 1% by weight.

23. A flame retardant resin composition as claimed in Claim 22, wherein said resin composition further comprises a polyphenylene ether in an amount of from 1 to 10 parts by weight per 100 parts by weight of said styrene resin.

24. A flame retardant resin composition as claimed in Claim 23, wherein said styrene resin has a reduced

viscosity $\eta SP/C$ of from 0.4 to 0.6 and said polyphenylene

ether has a reduced viscosity $\eta SP/C$ of from 0.3 to 0.6.

25. A flame retardant resin composition as claimed

in any one of Claims 22 to 24, wherein said aryl group

represented by R_1, R_2 and R_3 is selected from the group

consisting of a phenyl group, a benzyl group, and a cumyl

group.

26. A flame retardant resin composition as claimed

in any one of Claims 11 to 25, wherein said flame retardant

resin composition is a dripping flame retardant resin

composition.

27. A process for producing a resin composition as

claimed in any one of Claims 14 to 21 and 23 to 26, said

process comprising the steps of:

dividing a styrene resin into two batches;

preparing a first resin composition comprising one of

said two batches of said styrene resin and a polyphenylene

ether in an amount of not less than 50% by weight based on

the amount of said first resin composition;

melting said first resin composition at a temperature

of from 250°C to 350°C in a former stage of a twin-screw

extruder; and

melt-extruding said first resin composition with a

second resin composition comprising the other of said two

batches of said styrene resin and said flame retardant as

claims 23 to 25 at a temperature of from 200°C to 300°C in a latter stage of said twin-screw extruder.

28.   A process as claimed in Claim 27, wherein said twin-screw extruder has an L/D ratio of from 20 to 50, in which D represents an inner diameter of cylinder and L represents a length of screw, and a plurality of feed openings including a main feed opening and a side feed openings each disposed at different distances from a tip of said twin-screw extruder; and kneading zones are provided between said plurality of feed openings and between said tip of the twin-screw extruder and the feed opening nearest to said tip of the twin-screw extruder, said kneading zones each having a length of from 3D to 10D.

29.   A process for producing a resin composition as claimed in any one of Claims 14 to 21 and 23 to 26, said process comprising the steps of:

preparing a master batch comprising a resin composition comprising a polyphenylene ether and a flame retardant as claimed in any one of Claims 1 to 10 or as used in any one of claims 23 to 25, or preparing a master batch comprising said resin composition and a styrene resin and/or a rubber-modified styrene resin,

adding to said master batch the remainder of the components of asid resin composition as claimed in any one of Claims 14 to 21 and 23 to 26 to form a mixture, and

melt-kneading said mixture,

said master batch having a glass transition

temperature (Tg) of from 70°C to 100°C.

30. A low volatility aromatic phosphate flame

retardant, which exhibits a weight loss of from 0 to 10% by

5   weight at a temperature of 300°C and from 50 to 100% by

weight at a temperature of 400°C, in a heating test in

nitrogen, with a temperature rising rate of 40°C/min.

31. A low volatility aromatic phosphate flame

retardant as claimed in claim 30, wherein said flame

10   retardant is a flame retardant for a styrene resin.

Fig. 1

Total number of carbon atoms
in substituents

Fig. 2

Fig. 3

Fig. 4

Added weight parts of aromatic phosphate
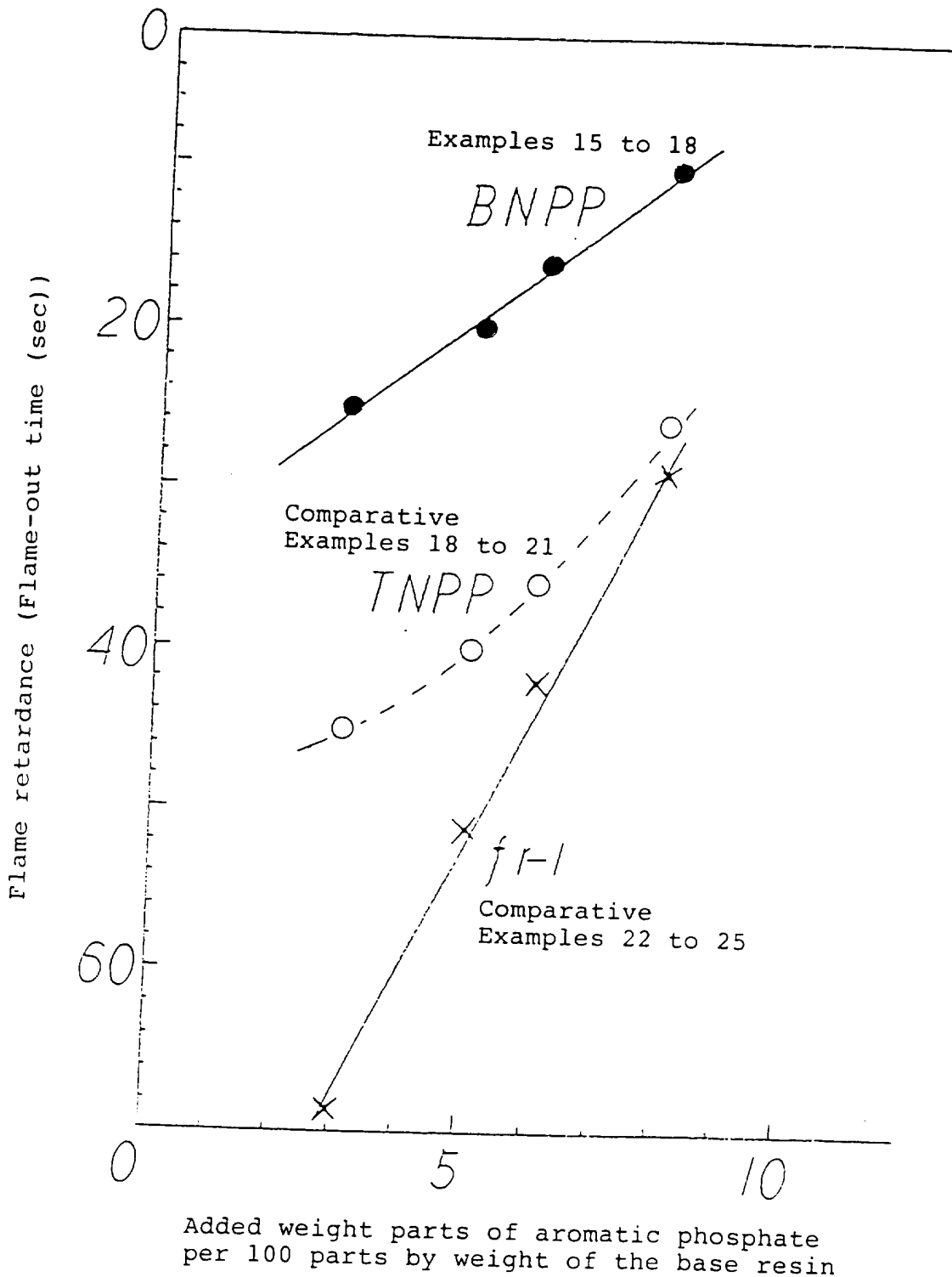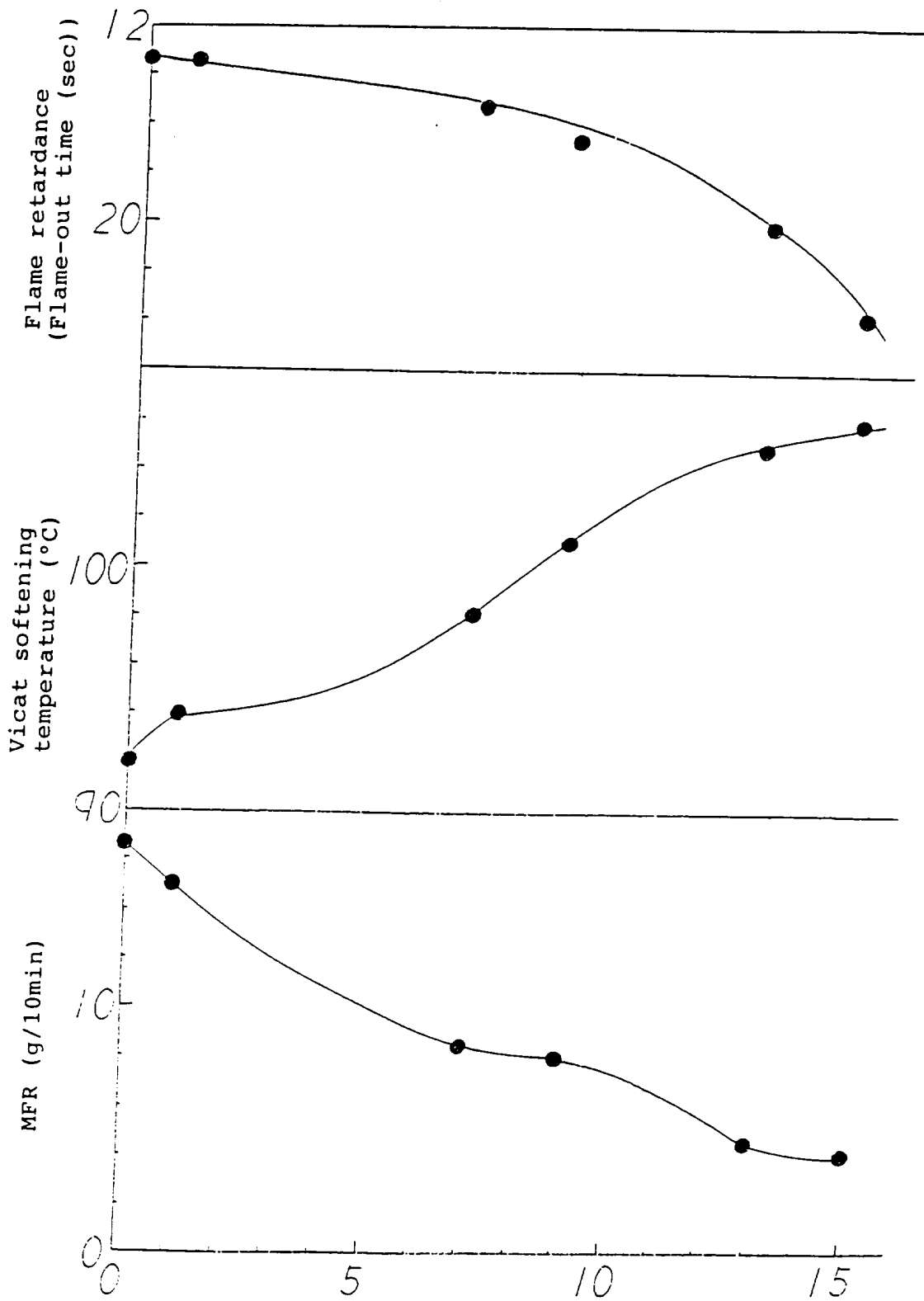per 100 parts by weight of the base resin
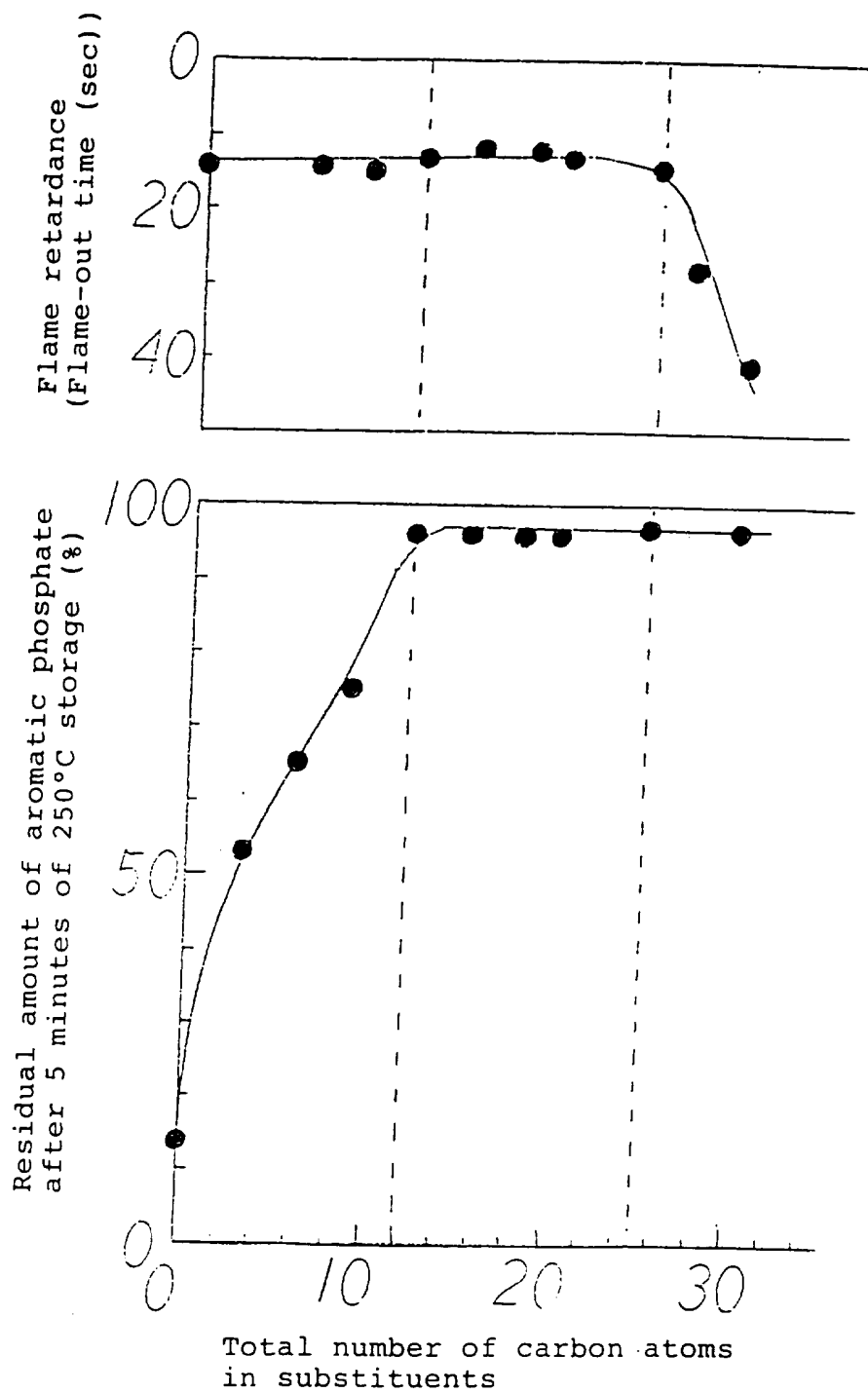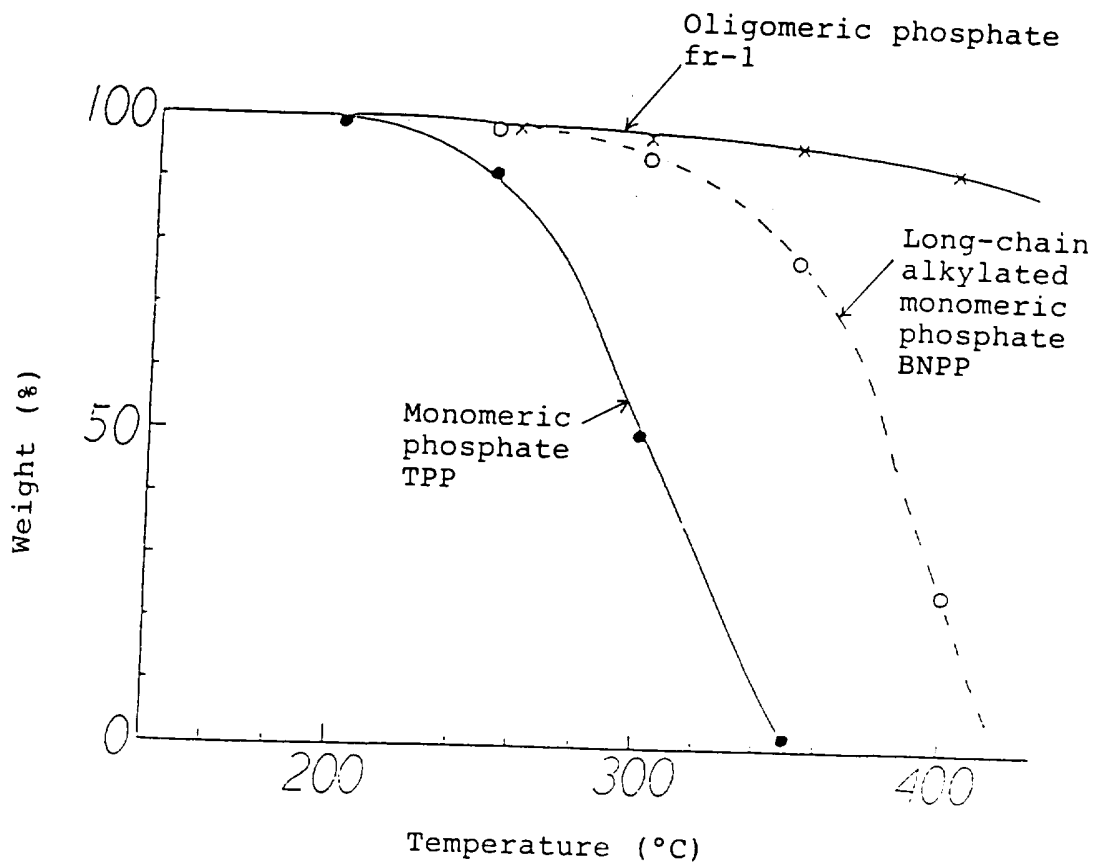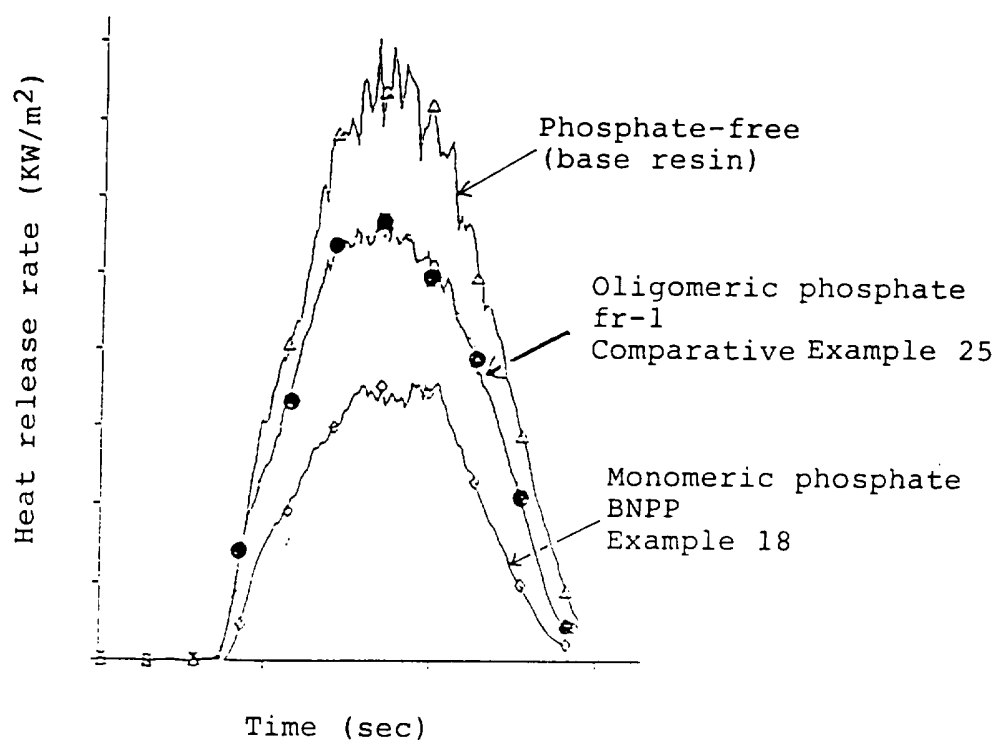
Fig. 5

Added weight parts of polyphenylene ether
per 100 parts by weight of the styrene resin

Fig. 6

HIPS-1/HIPS-7 weight ratio
in the base resin

Fig. 7

GPPS-1/GPPS-2 weight ratio
in the base resin

Fig. 8

Total number of carbon atoms in substituents
on the number average
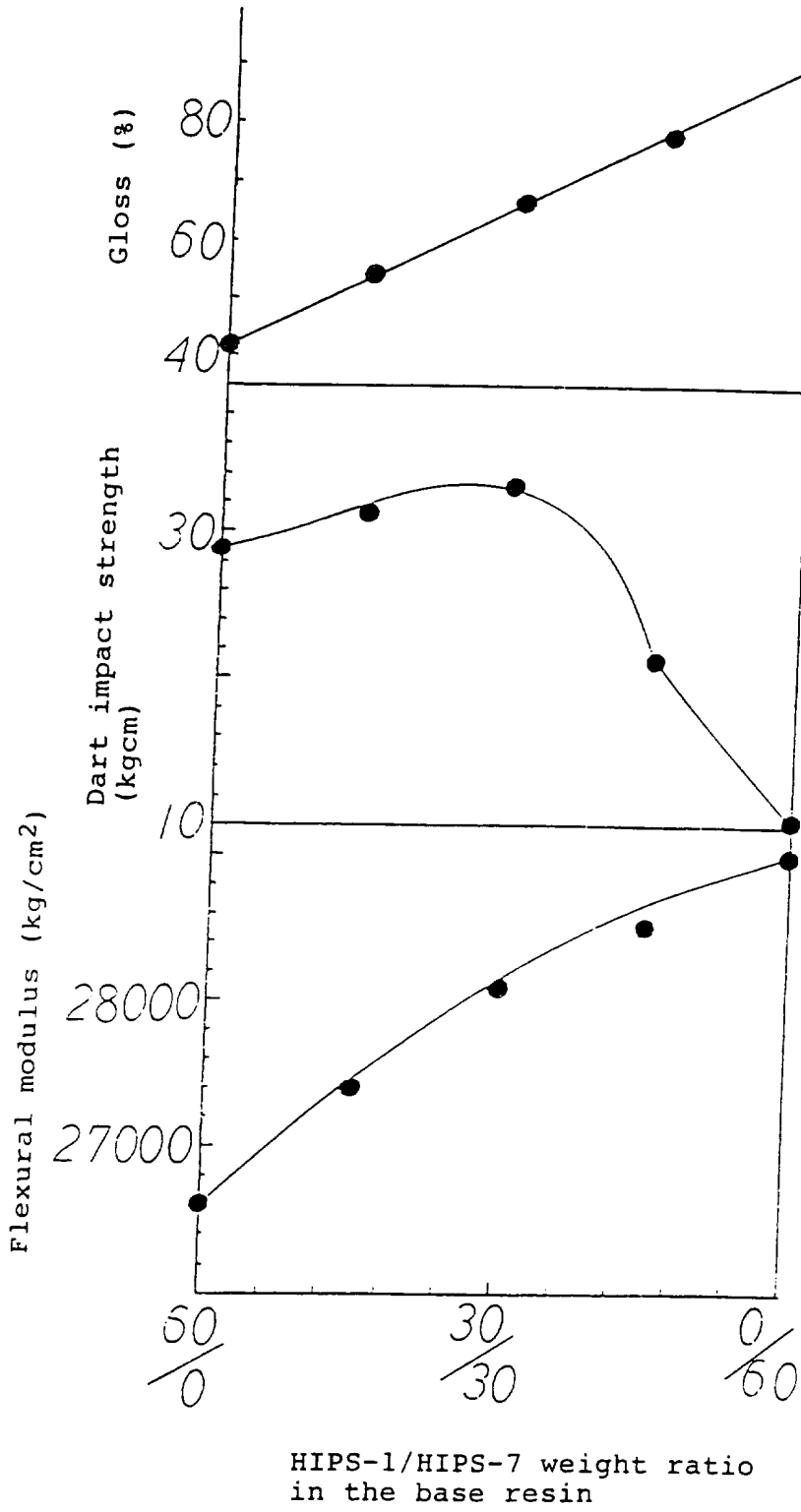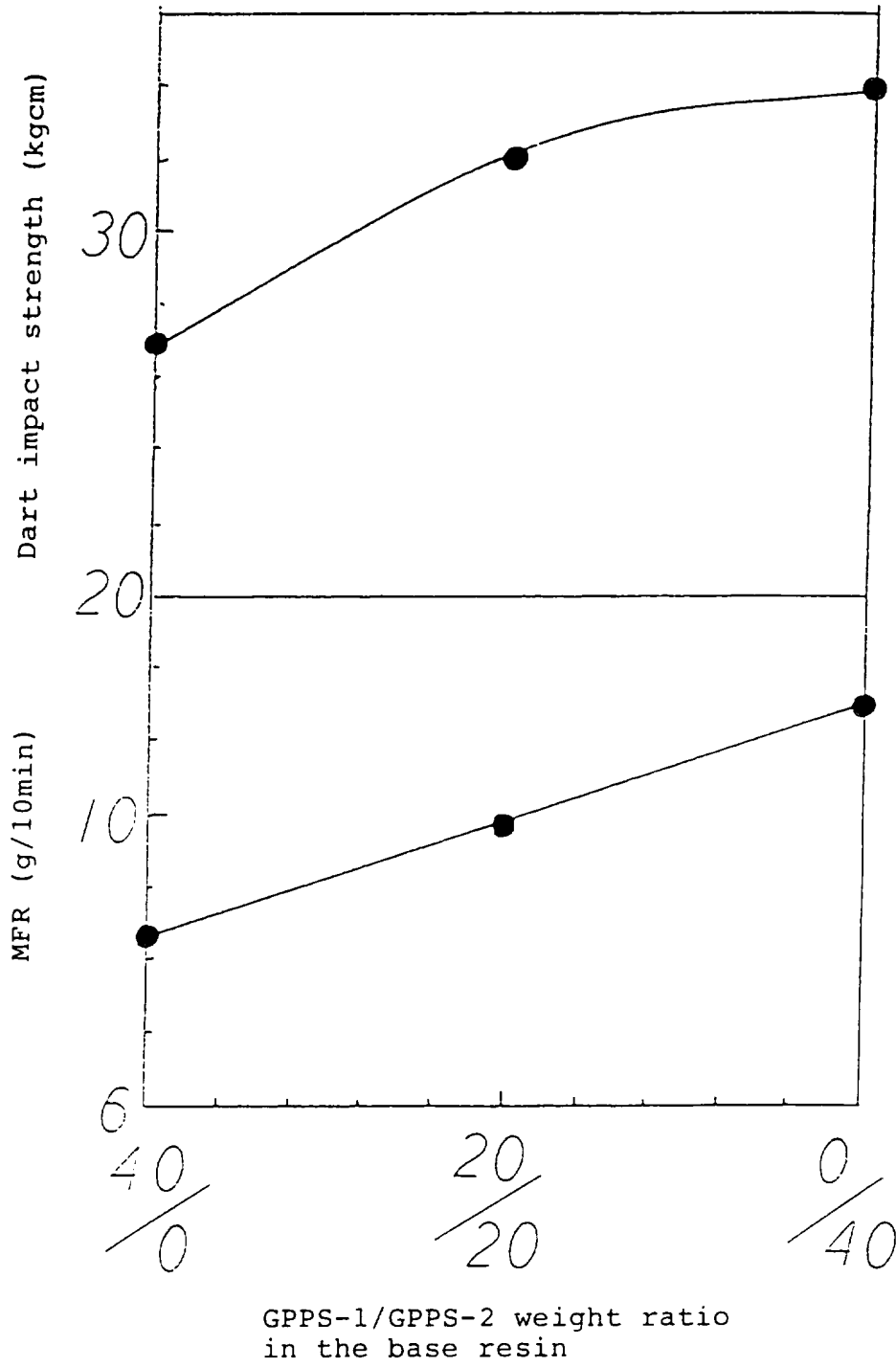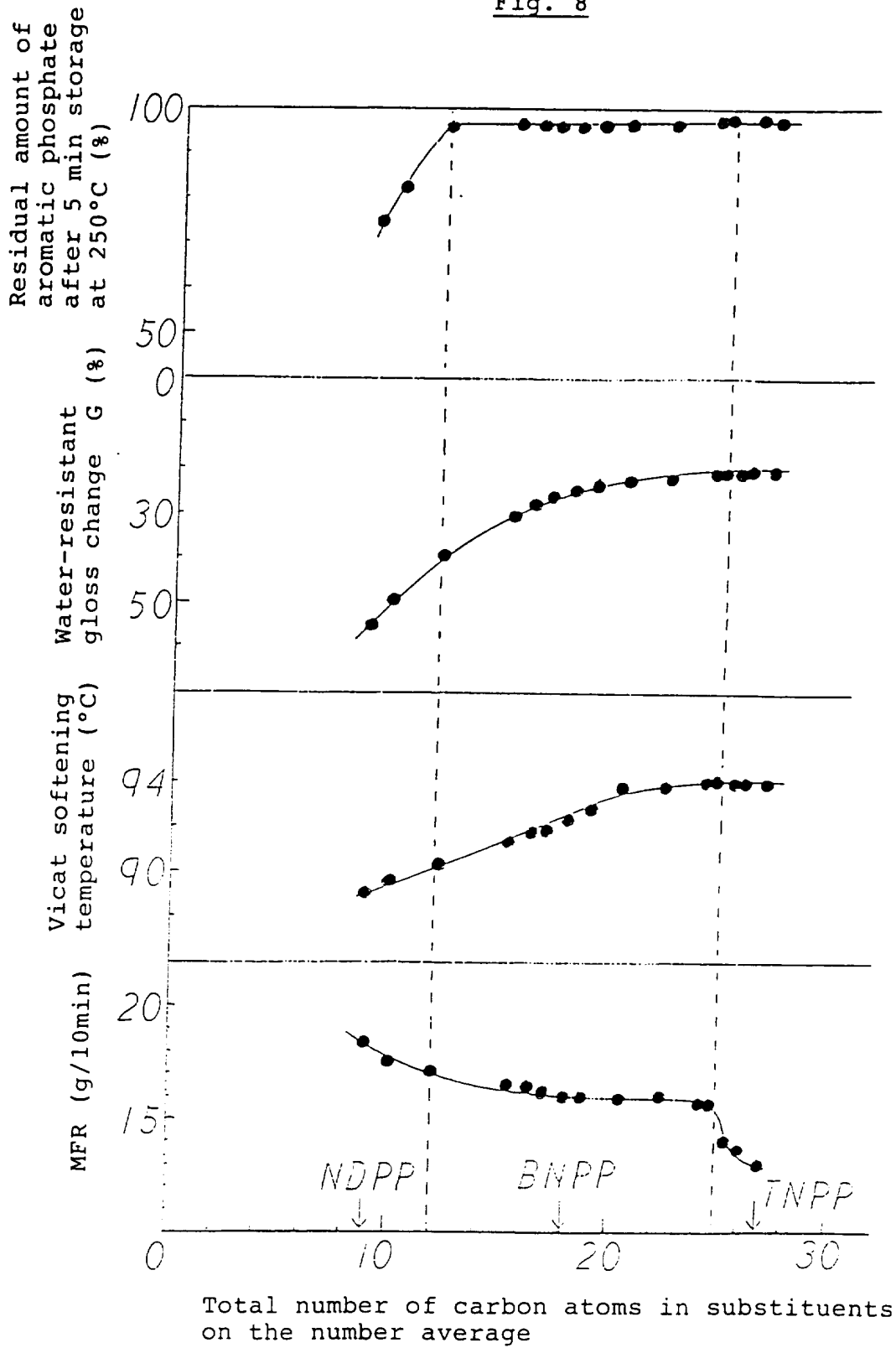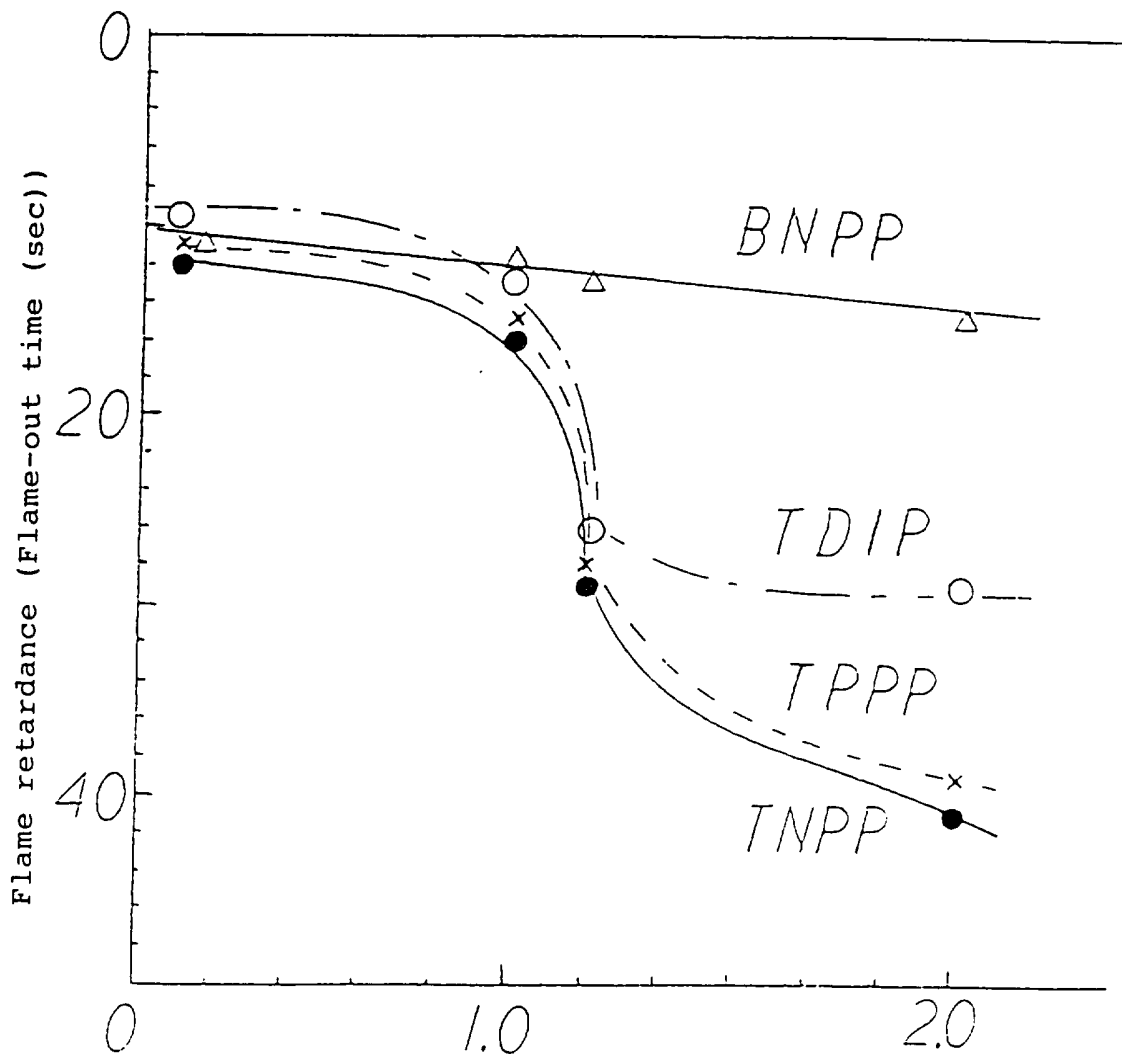
Fig. 9

Total content of remaining styrene monomer
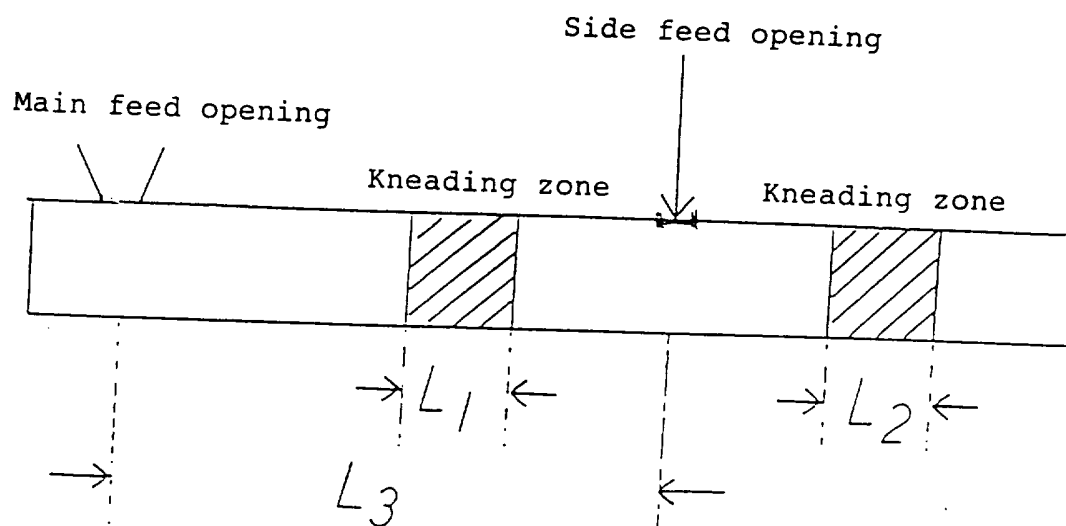and dimerization and trimerization products
of styrene

Fig. 10

Fig. 11
Feed Process

Main feed
Master batch
PPE, etc.)

Side feed
(resin, additive)

Side feed
(organo-
phosphorous
compound)

Fig. 12

Glass transition
temperature
of master batch

$94^{\circ}C$

$80^{\circ}C$

$104^{\circ}C$
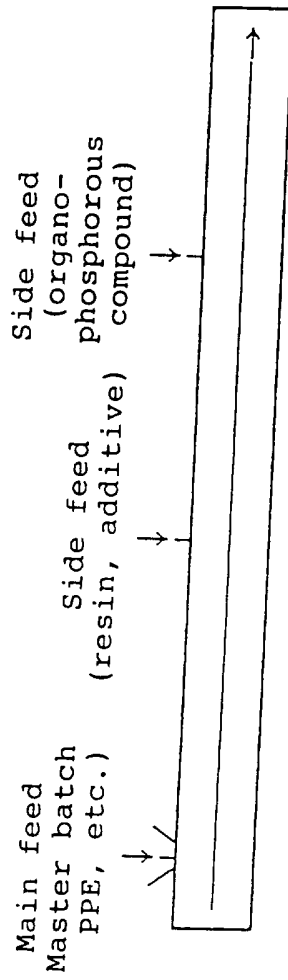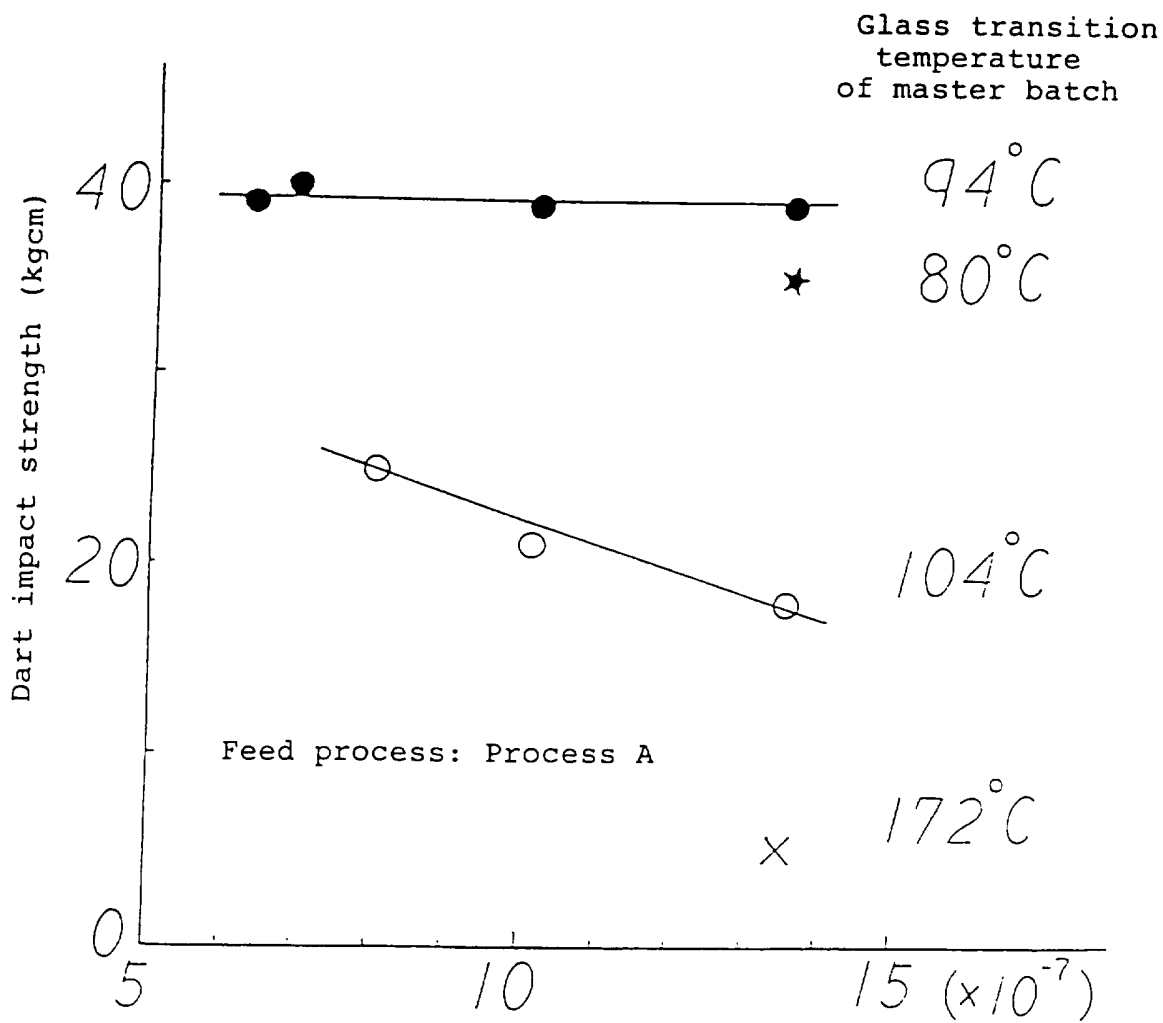
Feed process: Process A

$172^{\circ}C$

Dart impact strength (kgcm)

Kneading parameter = $\dfrac{\text{Extrusion factor}}{\text{Circumferential speed}}$

$= (Q/D^2)/\pi ND$

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08K5/523   C08L25/02   C08J3/22   C09K21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 876 298 (R.E. MALEC) 8 April 1975 see column 2, paragraph 4 - paragraph 5; examples see column 4, line 26 - line 28 see column 4, line 49 - line 53 ---	1-3
A	EP,A,0 640 655 (BAYER AG) 1 March 1995 see page 6, line 33 - line 37 see page 8, line 44 - line 49 see claims 1-6 ---	1,11,14, 19,21
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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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

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"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

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 1996	-2.07.96

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page 1 of 3

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A	EP,A,0 595 121 (BASF AG) 4 May 1994 see page 2, column 2, line 40 - line 42 see page 3, column 3, line 12 - line 16 see page 3, column 4, line 42 see page 3, column 4, line 51; claims 1,7 ---	22
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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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