Title: METHOD AND COMPOSITION FOR IMPROVING GAS BARRIER PROPERTIES OF POLYMERIC CONTAINERS AND FILMS

Abstract: A polymer composition and method for reducing the permeability of gases through molded polymeric containers and films by incorporating into the polymer from which the container or film is formed an effective amount of a barrier-enhancing additive, such as monoesters of hydroxybenzoic acid and hydroxynaphthoic acid.
TITLE
METHOD AND COMPOSITION FOR IMPROVING GAS BARRIER
PROPERTIES OF POLYMERIC CONTAINERS AND FILMS

CROSS REFERENCE(S) TO RELATED APPLICATION(S)
This application claims priority benefit from U.S. provisional patent
application no. 60/148,537 filed August 12, 1999.

BACKGROUND OF THE INVENTION
The present invention is a polymer composition and method for improving the
gas barrier performance of polymeric containers and films, and particularly containers
for food and beverages which are molded from thermoplastic polyester polymers.
More particularly, the invention is a polymer composition and method for reducing
the permeability of gases through molded polymeric containers, sheets and films by
incorporating into the polymer from which the container, sheet or film is formed an
effective amount of a barrier-enhancing additive of the type described herein.

The addition of small amounts of molecular additives to a base polymer can
result in antiplasticization of the polymer whereby the modulus of the polymer
increases below its glass transition temperature and its barrier to gas permeability can
improve. For example, Robeson describes the use of phenyl-2-naphthyl amine in
and various polychlorinated aromatic molecules in polycarbonate and in polyvinyl
disclose the use of tricresyl phosphate in polyphenylene oxide to lower the sorption of
carbon dioxide (and therefore its permeability). However, the need exists to improve
the gas barrier performance of polymer resins of the type currently used for molded
containers for food and beverages, and, in particular, poly(ethylene) terephthalate
(PET) thermoplastic polyester polymers used for producing injection stretch blow
molded bottles for packaging water, carbonated soft drinks and beer. Additives
selected from 4-hydroxybenzoates and related molecules of the type described herein
have not been suggested.
SUMMARY OF THE INVENTION

The present invention and the inventive features described herein reside in the discovery of certain barrier-enhancing additives for thermoplastic polymers. The invention is a polymer composition that contains one or more of the additives and a method for reducing gas permeability of shaped polymeric articles produced from such a composition, such articles being generally selected from containers, sheets and films.

The method comprises incorporating into the polymer an effective amount of a barrier-enhancing additive, or a mixture of barrier-enhancing additives, selected from the group consisting of:

(a) monoesters of hydroxybenzoic acid and hydroxynaphthoic acid of the formula (A)

\[
\text{ROC-}
\text{Ar}-\text{OH} \quad \text{(A)}
\]

\[
\text{ROC-}
\text{Ar}-\text{O}^{-} \quad \text{(AA)}
\]

\[
\left( \text{ROC-}
\text{Ar}-\text{O}^{-} \right)_{n}^{M^{+n}}
\]

wherein R is C₁ - C₈ alkyl, benzyl, phenyl or naphthyl; Ar is substituted or unsubstituted phenylene or naphthalene; or formula (AA) where M is a cation such as, but not limited to, sodium, ammonium, tetraalkyl ammonium, potassium, calcium, magnesium or zinc;

(b) diesters of hydroxybenzoic acid of the formula (B)

\[
\text{HO-}
\text{Ar}-\text{COR}_{1}\text{OC-}
\text{Ar}-\text{OH} \quad \text{(B)}
\]

\[
\left( \text{HO-}
\text{Ar}-\text{COR}_{1}\text{OC-}
\text{Ar}-\text{O}^{-} \right)_{n}^{M^{+n}}
\]
wherein Ar is as defined above, and R₁ is C₁ - C₈ alkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or more, benzyl, phenyl or naphthyl; or formula (BB) where M is as defined above.

(c) monoamides of hydroxybenzoic acid and hydroxynaphthoic acid of the formula (C)

\[
\begin{align*}
\text{RNHC} & \text{--Ar--OH} \\
\text{(C)}
\end{align*}
\]

\[
\begin{align*}
\text{RHN} & \text{C} \text{--Ar--O}^{-} \\
\text{(CC)}
\end{align*}
\]

\[
\begin{align*}
\left( \text{RHN} & \text{C} \text{--Ar--O}^{-} \right)^{nM^{+n}}
\end{align*}
\]

wherein R and Ar are as defined above; or formula (CC) where M is as defined above.

(d) diamides of hydroxybenzoic acid of the formula (D)

\[
\begin{align*}
\text{HO} & \text{--Ar--CNHR₂NHC} \text{--Ar--OH} \\
\text{(D)}
\end{align*}
\]

\[
\begin{align*}
\left( \text{HO} & \text{--Ar--CNHR₂NHC} \text{--Ar--O}^{-} \right)^{nM^{+n}}
\end{align*}
\]

wherein Ar is as defined above, and R₂ is C₁ - C₈ alkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or more, benzyl, phenyl or naphthyl; or formula (DD) where M is as defined above.
(e) ester-amides of hydroxybenzoic acid of the formula (E)

\[
\begin{align*}
\text{HO-Ar-COR}_3\text{NH-C-Ar-OH} & \\
\text{(E)}
\end{align*}
\]

where \( \text{Ar} \) is as defined above and \( \text{R}_3 \) is \( \text{C}_1-\text{C}_8 \) alkyl, \( \text{C}_1-\text{C}_8 \) dialkyl, \( (\text{CH}_2\text{CH}_2\text{O})_k\text{CH}_2\text{CH}_2 \) where \( k \) is 1 or greater, benzyl, phenyl or naphthyl, or


formula (EE) where \( M \) is as defined above. As used herein, an effective amount, i.e., the preferred range of barrier enhancing additive, is from 0.1% by wt. to 20% by wt. of the base polymer comprising the polymeric article.

Polymeric articles, and particularly extruded film or injection stretch blow molded polyester (e.g., PET) bottles, which contain one or more of the barrier-enhancing additives described herein, exhibit substantially reduced oxygen and carbon dioxide permeability values when measured according to ASTM D3985 and water vapor permeability values when measured according to ASTM F1249 in comparison to corresponding polymeric articles which contained no barrier-enhancing additives.

### Detailed Description of the Invention

The present invention resides in the discovery that oxygen, water vapor and carbon dioxide (\( \text{CO}_2 \)) permeability values for shaped polymeric containers and films can be substantially reduced by incorporating into the base polymer from which the articles are formed from about 0.1% by wt. up to about 20% by wt. of a barrier-enhancing additive of the type defined herein.

A uniform physical blend, or mixture, is prepared comprising the base polymer and one or more barrier-enhancing additives in the desired concentrations. As used herein with reference to the invention, the term “composition” is intended to mean a physical blend or mixture. Water-sensitive base polymers, such as, for
example, polyesters should preferably be thoroughly dried by heating under air or
nitrogen flow or vacuum as known to those experienced in the art. The mixture is
then heated and extruded or molded at a sufficiently high temperature to melt the base
polymer and provide for sufficient mixing of the additive or mixture of additives
within the base polymer matrix. By way of example using PET, such melt
temperature ranges from about 255°C to 300°C. The composition thus produced
comprises the barrier-enhancing additive (or mixture of such additives) substantially
in its (their) original molecular form; that is, only small amounts of barrier-enhancing
additive have been observed to react with the base polymer via trans-esterification or
other reaction mechanism typical of the functional groups present. It is preferred to
prepare and extrude or mold the polymer composition under conditions of relatively
low temperature and processing residence time which thereby minimizes the
opportunity for the barrier-enhancing additives to react with the base polymer. Best
performance in terms of desirable mechanical properties of polymeric containers and
films produced according to the invention is achieved when no more than about 10%
of the gas barrier-enhancing additive has reacted with the base polymer. As a
consequence of any reaction of a gas barrier-enhancing additive within the scope of
the invention with a base polymer, the molecular weight of the starting base polymer
may decrease.

The gas barrier-enhancing additives found to be most suitable for carrying out
the invention are selected from the group consisting of:

(a) monoesters of hydroxybenzoic acid and hydroxynaphthoic acid of the

\[
\begin{align*}
\text{ROC} & \text{Ar} \text{OH} \\
\text{(A)} \\
\text{(AA)} \\
\left(\text{ROC} \text{Ar} \text{O}^{-}\right)_n \text{M}^{+n}
\end{align*}
\]
wherein $R$ is $C_1$ - $C_8$ alkyl, benzyl, phenyl or naphthyl; $A_r$ is substituted or
unsubstituted phenylene or naphthylene; or formula (AA) where $M$ is a cation such as,
but not limited to, sodium, ammonium, tetraalkyl ammonium, potassium, calcium,
magnesium or zinc;

(b) diesters of hydroxybenzoic acid of the formula (B)

\[
\begin{align*}
&\text{HO} \quad \text{Ar} \quad \text{COR}_1 \quad \text{O} \quad \text{Ar} \quad \text{OH} \\
&\text{(B)} \\
&\left(\text{HO} \quad \text{Ar} \quad \text{COR}_1 \quad \text{O} \quad \text{Ar} \quad \text{O}^-\right)_n M^{+n}
\end{align*}
\]

wherein $A_r$ is as defined above, and $R_1$ is $C_1$ - $C_8$ alkyl, $(\text{CH}_2\text{CH}_2\text{O})_k\text{CH}_2\text{CH}_2$
where $k$ is 1 or more, benzyl, phenyl or naphthyl; or formula (BB) where $M$ is as
defined above.

(c) monoamides of hydroxybenzoic acid and hydroxynaphthoic acid of the
formula (C)

\[
\begin{align*}
&\text{R} \quad \text{NH} \quad \text{C} \quad \text{Ar} \quad \text{OH} \\
&\text{(C)} \\
&\left(\text{R} \quad \text{HN} \quad \text{C} \quad \text{Ar} \quad \text{O}^-\right)_n M^{+n}
\end{align*}
\]

wherein $R$ and $A_r$ are as defined above; or formula (CC) where $M$ is as defined
above.
(d) diamides of hydroxybenzoic acid of the formula (D)

\[
\begin{align*}
\text{HO} & \text{-Ar} \text{-CNHR}_2 \text{NH}_2 \text{-Ar} \text{-O} \text{-H} \\
\text{(D)}
\end{align*}
\]

\[
\left( \text{HO} - \text{Ar} - \text{CNHR}_2 \text{NH}_2 - \text{Ar} - \text{O}^- \right)_n \text{M}^{+n}
\]

wherein Ar is as defined above, and R_2 is C_1 - C_8 alkyl, (CH_2CH_2O)_kCH_2CH_2
where k is 1 or more, benzyl, phenyl or naphthyl; or formula (DD) where M is as
defined above.

(e) ester-amides of hydroxybenzoic acid of the formula (E)

\[
\begin{align*}
\text{HO} & \text{-Ar} \text{-COR}_3 \text{NH} \text{-Ar} \text{-O} \text{-H} \\
\text{(E)}
\end{align*}
\]

\[
\left( \text{HO} - \text{Ar} - \text{COR}_3 \text{NH} - \text{Ar} - \text{O}^- \right)_n \text{M}^{+n}
\]

where Ar is as defined above and R_3 is C_1 - C_8 alkyl, C_1 - C_8 dialkyl,
(CH_2CH_2O)_kCH_2CH_2, where k is 1 or greater, benzyl, phenyl or naphthyl, or
formula (EE) where M is as defined above.

The above-defined barrier-enhancing additives can be obtained from
commercial suppliers or they can be synthesized using established procedures.

Base polymers most suitable for use in practicing the invention comprise
thermoplastic homopolymers, copolymers (both block and random), and blends of
such thermoplastic polymers. Most suitable are polyester homopolymers and
copolymers. Among suitable polyester base polymers are those polymers which
contain structural units derived from one or more organic diacids (or their
corresponding esters) selected from the group consisting of terephthalic acid,
isophthalic acid, naphthalene dicarboxylic acids, hydroxybenzoic acids, hydroxynaphthoic acids, cyclohexane dicarboxylic acids, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecane dioic acid and the derivatives thereof, such as, for example, the dimethyl, diethyl, or dipropyl esters or acid chlorides of the dicarboxylic acids and one or more diols selected from ethylene glycol, 1,3-propane diol, naphthalene glycol, 1,2-propanediol, 1,2-, 1,3-, and 1,4-cyclohexane dimethanol, diethylene glycol, hydroquinone, 1,3-butanediol, 1,5-pentane diol, 1,6-hexane diol, triethylene glycol, resorcinol, and longer chain diols and polyols which are the reaction products of diols or polyols with alkylene oxides.

In a preferred embodiment of the invention the polyester base polymer is polyethylene terephthalate (PET), which includes PET polymer which has been modified with from about 2 mole% up to about 5 mole% of isophthalate units. Such modified PET is known as "bottle grade" resin and is available commercially as Melinar® Laser+ polyethylene terephthalate brand resin (E. I. du Pont de Nemours and Company, Wilmington, DE). As used hereinafter in illustrating the invention, the term PET will refer to commercially available "bottle grade" polyester resin.

**Preparation of Film and Container Samples**

Film samples are indicative of the improved gas barrier properties obtainable from the invention. Such film samples were generated from physical blends of a base polymer and a selected additive from among those described herein, and the samples were either compression molded or extrusion cast using a co-rotating twin screw extruder with a slit die, typically having a 0.38 mm gap, a quench roll, and a vacuum port on the front barrel section, with barrel, adapter, and die temperatures set at 240°C to 275°C depending on the polymer composition being used. Melt temperatures were measured with a thermocouple, and, for samples prepared using a twin screw extruder, melt temperatures were typically about 15°C to 20°C above the set temperature. In a few instances as noted, a transfer line, in which static mixers were installed within the line in place of a compounding screw, was used along with a slit die. Films were typically 0.05 to 0.25 mm thick. The thick films were subsequently stretched biaxially simultaneously to 3.5X by 3.5X using a Long stretcher at 90°C, 9000%/minute unless otherwise noted.
For fabricating bottles, 26g preforms were injection molded using a Nissei
ASB 50 single stage injection stretch blow molding machine with barrel temperatures
set at about 265°C and with a total cycle time of about 30 seconds. The preforms
were immediately blown into 500 mL round-bottomed bottles with a blow time of
5 seconds. All other pressure, time and temperature set-points were typical for
commercially available PET bottle resin.

Tensile bars 1/8" thick were molded using a 6oz. injection molding machine
with the following machine set-up: barrel temp: 255°C, mold temp: 20°C/20°C, cycle
time: 20 sec/20 sec, injection pressure: 5.5 MPa, RAM speed: fast, screw speed:
60 rpm, and back pressure: 345 kPa.

Analytical Procedures

NMR Spectrometry

Samples for 1H NMR were dissolved in tetrachloroethane-d2 at 130°C.
Spectra were acquired at 120°C at 500 MHz.

Thermal Analysis

Differential Scanning Calorimetric data were acquired at 2°/min on a TA
Instruments calorimeter.

Permeability

Oxygen permeability values (OPV) were measured for each sample according
to ASTM procedure D3985 at 30°C, 50% RH on an Ox-Tran 1000 instrument from
Modern Controls, Inc. Carbon dioxide permeability was measured at 25°C and 0%
RH on a Permatran CIV instrument, also from Modern Controls, Inc. Water vapor
permeability was measured at 37-38°C, 100% RH on a Permatran-W600 instrument,
also from Modern Controls, according to ASTM procedure F1249.
Intrinsic Viscosity

Intrinsic viscosity values were determined from 0.4 wt% solution of polymers or polymer blends in a 1:1 (by weight) mixture of methylene chloride and trifluoroacetic acid at 20°C.

EXAMPLES

Example 1

Films comprising commercially available PET resin (Melinar® Laser+ PET brand resin) as the base polymer plus a barrier additive were prepared by a variety of methods as follows: melt pressing (M), extrusion compounding through a slit die (E), and transfer line mixing (T) into a slit die, and noted below in the table. Compositions are indicated in Table 1. After extrusion, films were simultaneously biaxially stretched to 3.5X by 3.5X at 90°C and at a rate of 9000%/min. Oxygen permeation values (OPV) were measured according to ASTM procedure D3985 at 30°C, 50% relative humidity. Weight percent of the additive in the resin was assayed by NMR; where such analysis was not possible, nominal values (i.e., amounts initially mixed into the resin) are noted. In each case, both in unstretched and stretched films, the OPV was lower in films which contained a barrier-enhancing additive according to the invention than typical PET values (Control values, Table 1). OPV units are cc-mils/100 sq. in-24 hr-atm.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation*</th>
<th>Additive</th>
<th>Wt % (NMR)</th>
<th>OPV: Unstretched</th>
<th>OPV: Stretched</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>E</td>
<td>None</td>
<td>0</td>
<td>11.08**</td>
<td>7.23**</td>
</tr>
<tr>
<td>A</td>
<td>M</td>
<td>Methyl 4-hydroxybenzoate</td>
<td>2.48</td>
<td>7.07</td>
<td>3.48</td>
</tr>
<tr>
<td>B</td>
<td>T</td>
<td>Methyl 4-hydroxybenzoate</td>
<td>5.74</td>
<td>3.76</td>
<td>3.56</td>
</tr>
<tr>
<td>C</td>
<td>T</td>
<td>Methyl 4-hydroxybenzoate</td>
<td>3.49</td>
<td>7.14</td>
<td>3.69</td>
</tr>
<tr>
<td>D</td>
<td>T</td>
<td>Methyl 4-hydroxybenzoate</td>
<td>1.55</td>
<td>8.17</td>
<td>4.70</td>
</tr>
<tr>
<td>E</td>
<td>T</td>
<td>Methyl 4-hydroxybenzoate</td>
<td>0.66</td>
<td></td>
<td>5.91</td>
</tr>
<tr>
<td>F</td>
<td>E</td>
<td>Ethyl 4-hydroxybenzoate</td>
<td>3.71</td>
<td>5.42</td>
<td>4.14</td>
</tr>
<tr>
<td>G</td>
<td>E</td>
<td>n-Propyl 4-hydroxybenzoate</td>
<td>2.90</td>
<td>7.91</td>
<td>4.74</td>
</tr>
<tr>
<td>H</td>
<td>E</td>
<td>i-Propyl 4-hydroxybenzoate</td>
<td>6.00 (nominal)</td>
<td></td>
<td>4.01</td>
</tr>
<tr>
<td>I</td>
<td>M</td>
<td>Benzyl 4-hydroxybenzoate</td>
<td>5.88 (nominal)</td>
<td>8.87</td>
<td>3.99</td>
</tr>
<tr>
<td>J</td>
<td>M</td>
<td>Phenyl 4-hydroxybenzoate</td>
<td>5.55 (nominal)</td>
<td>7.71</td>
<td>3.82</td>
</tr>
<tr>
<td>K</td>
<td>E</td>
<td>Phenyl hydroxynaphthoate</td>
<td>5 (nominal)</td>
<td>8.49</td>
<td>4.47</td>
</tr>
</tbody>
</table>

* Preparation methods: E = extrusion compounded then extrusion through a slit die to make film; M = melt-pressed film; T = transfer line with static mixers then extrusion through a slit die to make film.

** For unstretched PET film, the control OPV is the mean of values for seven different samples, each run in duplicate; the standard deviation is 0.49. For stretched film, the control OPV is the mean of values for 27 different samples, each run in duplicate; the standard deviation is 0.41.

**Example 2**

Films prepared from commercially available PET resin (Melinar® Laser+ brand PET resin) which contained zero or nominally 2 wt% of the sodium salt of
methyl 4-hydroxybenzoate were extruded using a twin screw extruder. Oxygen permeability values were determined for both as-cast and biaxially stretched films, as in Ex. 1. Films were stretched to 3.5X by 3.5X at 9000%/min, 100°C. The OPV for the stretched film containing the additive was 5.18 cc-mils/100 sq. in-24 hr-atm stretched, versus 6.56 for stretched PET film without an additive; the additive therefore produced a 26.6% improvement in oxygen barrier performance.

**Example 3**

Poly(propylene terephthalate) (3GT) films containing zero and nominally 3 wt% methyl 4-hydroxybenzoate (MHB) were prepared using a twin screw extruder and a barrel setting of 240°C. Films containing no MHB and nominally 3 wt% MHB were stretched 3X by 3X at 55°C and 53°C respectively. Oxygen permeability values for the 3GT films containing MHB were 4.72 cc-mil/100 sq. in-24 hr-atm for cast film and 3.59 cc-mil/100 sq. in-24 hr-atm for stretched film, versus the 3GT control OPV values of 8.56 for as-cast film and 5.30 for stretched film. Water vapor permeability at 38°C for as-cast films containing MHB was 2.22 g-mil/100 sq. in-24 hr and 1.95 g-mil/100 sq. in-24 hr for stretched film, versus the 3GT control values of 3.50 for as-cast film and 2.24 for stretched film.

**Example 4**

A blend of MHB with PET (IV 0.86) was prepared via twin-screw extrusion at 245°C. The resulting blend, which was a concentrate, had an IV of 0.86 dL/g, and contained 6.9% MHB by NMR analysis. The blend was dried overnight at 100°C under vacuum and combined with standard commercial PET bottle resin (IV 0.83 dL/g, dried 6 hours at 150°C). 26g sample preforms were then injection molded using a Nissei ASB 50 single stage injection stretch blow molding machine, using barrel temperatures of about 265°C and a total cycle time of approximately 30 seconds. The preforms were immediately blown into 500 mL round-bottomed bottles with a blow time of 5 seconds. All other pressure, time and temperature set-points were typical for standard PET bottle resin. A control set of bottles made only
of the standard PET bottle resin (IV 0.83, dried 6 hours at 150°C) was prepared under the same conditions. The oxygen permeation value for panels cut from bottles containing 1.97 wt% methyl 4-hydroxybenzoate (‘MHB’) was determined to be 3.69 cc-mils/100 sq. in-24 hr-atm versus 5.73 for a control PET bottle panel. Carbon dioxide permeation values were 9.65 cc-mil/100 sq. in-24 hr-atm. for the bottle with MHB and 14.62 for the control panel.

**Example 5**

Commercially available PET film containing 4 wt% MXD-6 6007 nylon (Mitsubishi Gas Chemical Corp.) and, nominally, 3 wt% MHB was extruded along with a PET control film. The films were biaxially stretched 3.5X by 3.5X as in Example 1. The OPV for the film containing the additives was 2.59 cc-mils/100 sq. in-24 hr-atm, versus the control film’s OPV of 7.14.

**Example 6**

A diester of p-hydroxybenzoic acid (‘HBA’) (corresponding to Formula B where R₁ = CH₂CH₂) was synthesized from the reaction of stoichiometric mixtures of HBA and ethylene glycol in diphenyl ether with the catalyst butyl stannoic acid. PET films containing 0 and 4.55 wt% of this diester were extruded and then stretched as in Example 1. The OPV of the film containing the diester was 3.93 cc-mils/100 sq. in-24 hr-atm, and the OPV of the PET film without the diester was 7.32 cc-mils/100 sq. in-24 hr-atm.

**Example 7**

The benzamide of HBA (corresponding to Formula C where R = phenyl) was synthesized from the reaction of MHB with benzylamine. An extruded PET film containing a nominal 3 wt% of this benzamide and stretched as in Example 1 exhibited an OPV of 5.00 cc-mil/100 sq. in-24 hr-atm, vs. a PET control film which had an OPV of 6.94.
Example 8

The diamide of HBA (corresponding to Formula D where $R_1 = \text{CH}_2\text{CH}_2$) was synthesized from the reaction of 4-acetoxybenzoyl chloride with ethylene diamine, followed by basic hydrolysis of the acetate groups. An extruded PET film containing a nominal 3 wt% of this diamide and stretched as in Example 1 exhibited an OPV of 5.46 cc-mil/100 sq. in-24 hr-atm whereas a PET control film exhibited an OPV of 7.79.

Example 9

A diester of HBA and triethylene glycol was synthesized from the reaction of stoichiometric mixtures of HBA and triethylene glycol in diphenyl ether with the catalyst butyl stannic acid. PET film containing 6.49 wt% of this diester (determined by NMR) was extruded and stretched as in Example 1. The OPV for this film was 4.0 cc-mil/100 sq. in-24 hr-atm whereas a PET control film exhibited an OPV of 7.04.

Example 10

A blend of 97 wt% dried PET resin (Melinar® Laser+ brand PET resin) and 3 wt% methyl 4-hydroxybenzoate was mixed thoroughly and added to the hopper of a 6 oz. injection molding machine. Standard 1/8" thick tensile bars were molded with the following machine set-up: barrel temp 255°C, mold temp: 20°C/20°C, cycle time: 20 sec/20 sec, injection pressure: 5.5 MPa, RAM speed: FAST, screw speed: 60 rpm, and back pressure: 345 kPa. Intrinsic viscosity was measured on sections which were cut from the center of the bars using a 0.4% solution in 1:1 TFA: CH$_2$Cl$_2$ at 19°C. The I.V. was 0.73 dL/g vs. a control PET resin sample molded under identical conditions which had an I.V. of 0.73 dL/g.

In contrast, the I.V. of the bottle from Example 4, containing 1.97 wt% MHB and prepared from a pre-compounded MHB/PET concentrate, was 0.464 dL/g, and the control PET bottle I.V. was 0.76 dL/g. This example demonstrates that degradation of the polymer composition’s molecular weight (as evidenced by I.V.) can be avoided by selection of appropriate processing conditions.
**Example 11**

Laser+ PET films containing 0 to 3.46 wt% MHB were prepared by extrusion compounding. Two of these were also biaxially stretched as in Example 1. Water vapor permeabilities (g-mil/100 sq. in - 24 hr) at 38°C, 100% relative humidity are tabulated below.

<table>
<thead>
<tr>
<th>MHB Content (wt%)</th>
<th>Water Vapor Permeability, As-Cast Film</th>
<th>Water Vapor Permeability, Stretched Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.31</td>
<td>2.43</td>
</tr>
<tr>
<td>0.56</td>
<td>3.87</td>
<td>--</td>
</tr>
<tr>
<td>1.91</td>
<td>3.42</td>
<td>1.69</td>
</tr>
<tr>
<td>3.46</td>
<td>2.93</td>
<td>--</td>
</tr>
</tbody>
</table>

**Example 12**

Films of Lexan® 134r polycarbonate, Ultem® 1000 polyetherimide (both manufactured by General Electric), and Radel® polyethersulfone (manufactured by Boedeker Plastics, Inc.) containing 0 or nominally 5 wt% n-propyl p-hydroxybenzoate (PHB) were melt-pressed at 260, 270, and 270°C, respectively. Oxygen permeabilities (OPV) at 30°C are tabulated below.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>OPV, no PHB (cc-mil/100 sq. in. 24 hr)</th>
<th>OPV, nom. 5 wt% PHB (cc-mil/100 sq. in. 24 hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lexan® 134r polycarbonate</td>
<td>232.5</td>
<td>138.7</td>
</tr>
<tr>
<td>Ultem® 1000 polyetherimide</td>
<td>48.05</td>
<td>24.45</td>
</tr>
<tr>
<td>Radel® polyethersulfone</td>
<td>89.79</td>
<td>52.11</td>
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Example 13

Films of a copolymer of composition 7.4% poly(isosorbide terephthalate)-co-92.6% poly(ethylene terephthalate), prepared according to U.S. Patent No. 5,959,066, containing 0 to 3.85 wt% MHB were prepared by extrusion compounding, then biaxially stretched 3.5X by 3.5X at 90°C (95°C for 0% MHB), 9000%/min. Oxygen permeabilities are tabulated below.

<table>
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<th>MHB Wt%</th>
<th>OPV (cc-mil/100 sq. in/24 hr-atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.22</td>
</tr>
<tr>
<td>0.70</td>
<td>8.02</td>
</tr>
<tr>
<td>2.24</td>
<td>5.57</td>
</tr>
<tr>
<td>3.85</td>
<td>3.98</td>
</tr>
</tbody>
</table>
CLAIMS

WHAT IS CLAIMED IS:

1. A method for reducing gas permeability of polymeric containers, sheets and films which comprises incorporating into the polymer from which said containers, sheets and films are formed an effective amount of a barrier-enhancing additive or a mixture of barrier-enhancing additives selected from the group consisting of:

   (a) monoesters of hydroxybenzoic acid and hydroxynaphthoic acid of the formula (A)

   \[
   \text{ROC—Ar—OH} \quad \text{(A)}
   \]

   \[
   \left( \text{ROC—Ar—O}^- \right)^n \text{M}^{+n} \quad \text{(AA)}
   \]

   wherein R is C₁ - C₈ alkyl, benzyl, phenyl or naphthyl; Ar is substituted or unsubstituted phenylene or naphthylene; or formula (AA) where M is a cation such as, but not limited to, sodium, ammonium, tetraalkyl ammonium, potassium, calcium, magnesium or zinc;

   (b) diesters of hydroxybenzoic acid of the formula (B)

   \[
   \text{HO—Ar—COR₁OC—Ar—OH} \quad \text{(B)}
   \]

   \[
   \left( \text{HO—Ar—COR₁OC—Ar—O}^- \right)^n \text{M}^{+n} \quad \text{(BB)}
   \]
wherein Ar is as defined above, and R₁ is C₁ - C₈ alkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or more, benzyl, phenyl or naphthyl; or formula (BB) where M is as defined above.

(c) monoamides of hydroxybenzoic acid and hydroxynaphthoic acid of the formula (C)

\[
\begin{align*}
\text{RNHC} & \text{Ar} \text{OH} \\
\text{(C)} \\
\left(\text{RNHC} \text{Ar} \text{O}^{-}\right) & \text{M}^{+n}
\end{align*}
\]

wherein R and Ar are as defined above; or formula (CC) where M is as defined above.

(d) diamides of hydroxybenzoic acid of the formula (D)

\[
\begin{align*}
\text{HO} & \text{Ar} \text{CNHR₂NH} \text{Ar} \text{OH} \\
\text{(D)} \\
\left(\text{HO} \text{Ar} \text{CNHR₂NH} \text{Ar} \text{O}^{-}\right) & \text{M}^{+n}
\end{align*}
\]

wherein Ar is as defined above, and R₂ is C₁ - C₈ alkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or more, benzyl, phenyl or naphthyl; or formula (DD) where M is as defined above.
(e) ester-amides of hydroxybenzoic acid of the formula (E)

\[
\begin{align*}
\text{HO} & \text{Ar} \text{COR}_3 \text{NHC} \text{Ar} \text{OH} \\
\text{EE} & \\
\left( \text{HO} & \text{Ar} \text{COR}_3 \text{NHC} \text{Ar} \text{O}^- \right)_n\text{M}^{+n}
\end{align*}
\]

where Ar is as defined above and R₃ is C₁ - C₈ alkyl, C₁ - C₈ dialkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or greater, benzyl, phenyl or naphthyl, or formula (EE) where M is as defined above.

2. The method of Claim 1 wherein the barrier-enhancing additive or mixture of barrier-enhancing additives is incorporated into the polymer by physically mixing the components together and then extruding the resulting mixture through an extruder whereby the total concentration of barrier-enhancing additive in the extruded composition is from 0.1% by wt. up to about 20% by wt of the composition.

3. The method of Claim 2 wherein the polymer comprising the container, sheet or film is selected from thermoplastic homopolymers, random or block copolymers and a blend or blends of such homopolymers and copolymers.

4. The method of Claim 3 wherein the thermoplastic homopolymer or random or block copolymer is a polyester homopolymer or copolymer

5. A polymer composition comprising (1) a base polymer which is selected from thermoplastic homopolymers, random or block copolymers and a blend or blends of such homopolymers and copolymers and (2) an effective amount of a gas barrier-enhancing molecular additive or mixture of such gas barrier-enhancing molecular additives selected from the group consisting of:
   (a) monoesters of hydroxybenzoic acid and hydroxynaphthoic acid of the formula (A)
wherein R is C₁ - C₈ alkyl, benzyl, phenyl or naphthyl; Ar is substituted or unsubstituted phenylene or naphthylene; or formula (AA) where M is a cation such as, but not limited to, sodium, ammonium, tetraalkyl ammonium, potassium, calcium, magnesium or zinc;

(b) diesters of hydroxybenzoic acid of the formula (B)

\[
\text{HO--Ar--COR₁OC--Ar--OH} \quad \text{(B)}
\]

\[
\left( \text{HO--Ar--COR₁OC--Ar--O}^- \right)_{M^+}^{n} \quad \text{(BB)}
\]

wherein Ar is as defined above, and R₁ is C₁ - C₈ alkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or more, benzyl, phenyl or naphthyl; or formula (BB) where is M as defined above.

(c) monoamides of hydroxybenzoic acid and hydroxynaphthoic acid of the formula (C)

\[
\text{RNH--Ar--OH} \quad \text{(C)}
\]

\[
\left( \text{RNH--Ar--O}^- \right)_{M^+}^{n} \quad \text{(CC)}
\]
wherein R and Ar are as defined above; or formula (CC) where M is as defined above.

(d) diamides of hydroxybenzoic acid of the formula (D)

\[
\text{(D)} \quad \begin{array}{c}
\text{HO} \quad \text{Ar} \quad \text{CNHR}_2 \text{NHC} \quad \text{Ar} \quad \text{OH}
\end{array}
\]

\[
\text{(DD)} \quad \begin{array}{c}
\text{HO} \quad \text{Ar} \quad \text{CNHR}_2 \text{NHC} \quad \text{Ar} \quad \text{O}^-
\end{array} \quad M^{+n}
\]

wherein Ar is as defined above, and R₂ is C₁ - C₈ alkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or more, benzyl, phenyl or naphthyl; or formula (DD) where M is as defined above.

(e) ester-amides of hydroxybenzoic acid of the formula (E)

\[
\text{(E)} \quad \begin{array}{c}
\text{HO} \quad \text{Ar} \quad \text{COR}_3 \text{NHC} \quad \text{Ar} \quad \text{OH}
\end{array}
\]

\[
\text{(EE)} \quad \begin{array}{c}
\text{HO} \quad \text{Ar} \quad \text{COR}_3 \text{NHC} \quad \text{Ar} \quad \text{O}^-
\end{array} \quad M^{+n}
\]

where Ar is as defined above and R₃ is C₁ - C₈ alkyl, C₁ - C₈ dialkyl, (CH₂CH₂O)ₖCH₂CH₂ where k is 1 or greater, benzyl, phenyl or naphthyl, or formula (EE) where M is as defined above.

6. The polymer composition of Claim 5 in which the base polymer is a polyester homopolymer or copolymer which contains structural units derived from one or more organic diacids or their corresponding esters selected from the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acids, hydroxybenzoic acids, hydroxynaphthoic acids, cyclohexane dicarboxylic acids, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecane dioic acid and the
derivatives thereof which are the dimethyl, diethyl, or dipropyl esters or acid chlorides of the dicarboxylic acids and one or more diols selected from the group consisting of ethylene glycol, 1,3-propane diol, naphthalene glycol, 1,2-propanediol, 1,2-, 1,3-, and 1,4-cyclohexane dimethanol, diethylene glycol, hydroquinone, 1,3-butane diol, 1,5-pentane diol, 1,6-hexane diol, triethylene glycol, resorcinol, and long chain diols and polyols which are the reaction products of diols or polyols with alkylene oxides, and the gas barrier-enhancing molecular additive or mixture of such gas barrier-enhancing molecular additives are present in the polymer composition at a total concentration of from 0.1% by wt. up to about 20% by wt of the composition.

7. The polymer composition of Claim 6 in which the polyester homopolymer or copolymer is polyethylene terephthalate.

8. The polymer composition of Claim 5 in which the base polymer is selected from polycarbonates, polyetherimides and polyethersulfones.

9. An article of manufacture which is a sheet, a film or a container which is formed from the composition of Claim 5.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B65D65/38 C08K5/134 C08K5/138 C08K5/20 C08L67/02

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 7 B65D 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)
WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Relevant to claim No.</th>
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<td>A</td>
<td>US 3 575 931 A (SHERMAN NORMAN) 20 April 1971 (1971-04-20) examples</td>
<td>1,2,6,7</td>
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<tr>
<td>A</td>
<td>US 3 617 312 A (ROSE HENRY J) 2 November 1971 (1971-11-02) claims 1,2; example 3</td>
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<tr>
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<td>WO 95 23063 A (NESTE OY ;HAERKOENEN MIKA (FI); KUUSELA SEPPO (FI); LAIHO ERKKI (F) 31 August 1995 (1995-08-31) page 9, paragraph 5 examples 2-4</td>
<td>1-4,6</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:
*"A" document defining the general state of the art which is not considered to be of particular relevance
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*"O" document referring to an oral disclosure, use, exhibition or other means
*"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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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
"A" document of the same patent family

Date of the actual completion of the international search: 28 November 2000
Date of mailing of the international search report: 06/12/2000

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HD Rijswijk
Tel. (+31 –70) 340-2040, Tx. 31 651 epo nl, Fax. (+31 –70) 340-3016

Authorized officer: Engel, S
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<td>US 3516960 A</td>
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