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(54) Title: PHOTODEGRADATION AND HEAT-SEAL AGENTS FOR POLYMERIC MATRIX MATERIALS

(57) Abstract

A mixture of the anatase form of TiO₂ and a photodegradation polymer containing carbonyl groups along the polymer chain (especially an ethylene copolymer) synergistically enhances the photodegradation rate of polymeric matrix materials. Other additives such as rutile TiO₂ and/or other UV-sensitive or UV-absorbent or UV-stabilizing materials can be present to regulate the photodegradation rate. Furthermore, the presence of TiO₂ having an acid surface and said CO-containing polymer extends the heat seal temperature range of heat-sealable polymeric matrix material.
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PHOTODEGRADATION AND HEAT-SEAL AGENTS
FOR POLYMERIC MATRIX MATERIALS

The photodegradability and/or heat-seal range of polymeric matrix materials is controllably enhanced by incorporating therein TiO₂ and ethylene copolymers which have pendent carbonyl groups along the copolymer chain.

Photodegradation is the process whereby the ultraviolet radiation in sunlight attacks the chemical bonds in a chemical structure, such as plastics and polymers, thereby breaking the structure into smaller segments. This causes the structure to lose its physical strength, especially its ability to flex or stretch. The degradation process can continue the embrittlement and produce smaller and smaller pieces.

The photodegradation tendency of ethylene copolymers containing carbonyl groups (>C=O) is known and it is also known that the blending of such copolymers with other resins can cause the other resins to have a greater tendency to degrade by the effects of sunlight. A copolymer prepared by polymerizing ethylene with carbon monoxide is a well-known and preferred
example of a copolymer containing carbonyl groups; these copolymers have the \( \text{C} = \text{O} \) groups directly in the polymer chain. The ethylene/carbon monoxide copolymers include those which have other copolymerizable monomers contained in the polymer, such as acrylic acid, methacrylic acid, vinyl alkylates, alkyl acrylates, and even minor amounts of lower olefins, such as propylene or butylene. Patents showing the preferred method of making CO-containing ethylene copolymers include U.S. Patent 4,600,614 and U.S. Patent 4,601,948.

A European Patent Application published July 29, 1987 as European Patent No. 0230143 discloses that a photodegrading agent comprising a heavy metal dithiocarbamate or heavy metal dithiophosphate together with an ethylene/carbon monoxide polymer is useful for enhancing the photodegradation of an ethylene polymer, such as a linear low density polymer.

Another type of copolymer which has carbonyl oxygen groups, but which is less preferred in the present invention, is one prepared by copolymerizing ethylene with an alkyl vinyl ketone, such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone, or an alkyl isopropenyl ketone and the like; these copolymers have the carbonyl groups pendent from one of the carbons of the vinyl group which is directly in the polymer "backbone" chain. The location of the carbonyl groups in this type of copolymer chain structure can be illustrated generally by the following:

\[
\begin{align*}
\text{R}' \\
\text{(-CH}_2\text{-C-CH}_2\text{-CH}_2\text{-})_n \\
\text{C=O}
\end{align*}
\]
R where \( n \) is a plural number, \( R' \) is hydrogen or alkyl group, and where \( R \) is the alkyl group of the alkyl vinyl ketone or alkyl isopropenyl ketone, with the \( >C=O \) group connected directly to one of the carbon atoms of the vinyl group which is polymerized to become part of the chain.

For conciseness, the expression "CO-containing polymer", when used in this disclosure, is a reference to polymers which have \( >C=O \) groups along the polymer chain, whether it is directly in the chain or is connected to a carbon atom which is directly in the chain unless it is specifically identified as being one or the other.

The photodegradation properties of olefin polymers which contain carbonyl groups along the chain are disclosed in U.S. Patent 3,676,401 and U.S. Patent 3,860,538.

It is known that the anatase form of TiO\(_2\) will accelerate the photodegradation of polyethylene and polypropylene. The rutile form of TiO\(_2\) is relatively inactive with respect to the photodegradation of polymers to which it may be added, but it may be employed for other purposes, such as for pigmentation or thermal activity.

There is a recognized need for materials, especially packaging resins, which are more readily decomposed by sunlight. This includes such items as disposable diaper materials, trash bags, garbage bags, grocery bags, food wraps, beverage cartons, beverage can "loop holders", portions of sanitary napkins, disposable gloves, wiping rags, and other discardable products.
For purposes of distinguishing between (1) the polymers or copolymers used herein as part of the photodegradating agents or and (2) the polymeric matrix materials into which the photodegradating agents are added, the latter will be referred to herein as "matrix resins". Thus unless otherwise identified, the term "polymers or copolymers" refers herein to portions of the photodegradating agents, and which are also useful in enhancing the photodegradation of the matrix resins.

A first aspect of the invention is a photodegrading agent comprising a blend of anatase TiO2 and at least one photodegrading polymer containing carbonyl CO groups along the polymer chain.

A second aspect of the invention is a process of synergistically enhancing the photodegradation rate of photodegradation polymers containing carbonyl groups along the polymer chain; the said process comprising incorporating the anatase form of TiO2 therein.

It has now been found, unexpectedly, that there is a synergistic effect in the combined use of a CO-containing polymer and anatase titanium oxide, TiO2, as an agent for the photodegradation of matrix resins. The combination exhibits accelerated rates of photodegradation. When the combination is added, for example as a masterbatch, to a matrix resin the photodegradation of the matrix resin is desirably accelerated. It has also been found that by employing various predetermined amounts of the CO-containing polymer, anatase TiO2, rutile TiO2, and UV stabilizers which are added to resins, one can exercise appreciable control on the amount of pigmentation, and photodegradation rate of various formulations. We have
not found the rutile form of TiO$_2$ to exhibit the enhancement of photodegradation that is exhibited by the anatase form of TiO$_2$ and we have determined that one can use predetermined mixtures of anatase TiO$_2$ and rutile TiO$_2$ to achieve various degrees of pigmentation having various degrees of photosensitivity.

Furthermore, we have also found that the heat-seal range of the matrix resin is beneficially broadened by the presence therein of the above TiO$_2$/CO-containing polymer agents; in heat-sealing using radiant and or conduction heat it does not matter (vis-a-vis the heat seal range) whether the TiO$_2$ is rutile or anatase, though it does matter if heating is being done using RF energy, especially MW energy, to cause heating of the material.

The present invention involves the following listed related, identifiable aspects or embodiments:

1. A blend containing anatase TiO$_2$ and at least one CO-containing polymer, said blend having a beneficial rate of photodegradation. An ethylene copolymer containing copolymerized carbon monoxide (CO) in the polymer chain backbone is the preferred type of CO-containing polymer.

2. A blend containing predetermined amounts of anatase TiO$_2$, at least one CO-containing polymer, and optionally rutile TiO$_2$ and/or UV stabilizer, said blend exhibiting a predetermined regulated rate of photodegradation.

3. A blend of a matrix resin which contains anatase TiO$_2$ and at least one CO-containing polymer.

4. A blend of a matrix resin which contains predetermined amounts of anatase TiO$_2$, at least one CO-containing polymer, and optionally rutile TiO$_2$ and/or UV
stabilizer.

5. A process of synergistically enhancing the photodegradation rate of CO-containing polymers by incorporating the anatase form of TiO₂ therein.

6. A process of accelerating the photodegradation rate of a matrix resin, said process comprising incorporating into the matrix resin a photodegrading composition (or "agent") comprising anatase TiO₂ and at least one CO-containing polymer.

7. A process of providing a predetermined regulated rate of photodegradation to a matrix resin, said process comprising blending the matrix resin with predetermined amounts of anatase TiO₂, at least one CO-containing polymer and optionally rutile TiO₂, and/or a UV stabilizer.

The photodegradation rate of CO-containing polymers is synergistically accelerated by the addition thereto of the anatase form of TiO₂ and is not merely a numerically additive effect of the two ingredients. That, in itself, is beneficial in the preparation of articles which can be made directly from an anatase TiO₂/polymer blend and relatively fast photodegradation is desirably obtained.

The mixture of anatase TiO₂/CO-containing polymer is also used as an agent to provide a faster photodegradation rate to articles such as resin films, filaments, fibers, sheets, slabs, containers or other configurations prepared from matrix resins. The agent may, as a "masterbatch" of TiO₂/CO-containing polymer, be blended with the matrix resin in which the accelerated rate of photodegradation is desired. The carbonyl-containing polymer and the TiO₂ can be added separately to the matrix resin, but are beneficially and
preferably mixed together to form a photodegrading agent which is then added to the resin. Optionally, other additives and/or degradation accelerators and/or photostabilizers and/or photosensitizers may also be employed along with the agent of this invention either by way of having the photodegradation agent added to matrix resins which contain the said optional ingredients, or by way of adding the optional additives to matrix resins which contain the photodegradation agents, or by adding them to the matrix resin at substantially the same time.

Within the ambit of the present invention the matrix resins to which a photodegrading property are desired to be imparted or accelerated may be resins which are used in making packaging materials, especially those which are usually intended to be discarded after their first use. Examples of matrix resins are polyolefins, polyesters, polyurethanes, polyamides, polyepoxides, polyacrylates and polycarbonates. Such articles as garbage bags, grocery bags, tampon-type applicators, wipe-cloths, hygiene products, disposable diapers, sanitary napkins, food-wrapping, food cartons, can holders, beverage overwraps, beverage containers, beer can "loop carriers", and the like, often comprise or include resins which can be caused to be more rapidly photodegraded by sunlight. Of special interest in this regard are those resins which are prepared from olefin monomers and/or vinyl monomers, such as ethylene, propylene, butene, styrene, vinyl acetate, vinyl halide, and derivatives of these or other such monomers which are used in making plastics and which are often used as discardable packaging materials. Resins prepared from olefins and mixtures of olefins, such as low density
branched polyethylene (LDPE), linear low density
polyethylene (LLDPE) and high density linear
polyethylene (HDPE) as well as styrene polymers and
copolymers are of particular interest as the matrix
resins in this invention. LLDPE resins are of special
interest considering, among other things, the strength
and impact resistance they exhibit which makes them
popular in the making of garbage bags and trash bags.
Compositions comprising HDPE are particularly useful for
preparing discardable molded articles. Compositions
comprising LLDPE or LDPE are particularly useful for
preparing discardable melt-extruded films. Compositions
comprising styrenic polymers or copolymers are
particularly useful for preparing discardable foams.

The titanium oxide, TiO₂, which exhibits a
synergistic effect when combined with CO-containing
polymers is of the crystalline form known as anatase.
Throughout this disclosure the TiO₂ is the anatase form
unless stated otherwise.

The CO-containing polymer used as a
photodegrading agent, in conjunction with the TiO₂, may
be any thermoplastic polymer which has carbonyl groups
along the polymer chain and which is either compatible
with, or can be compatibilized with, the resin into
which it is to be blended. Compatibilizing may be
accomplished, e.g., by the addition of a compatibilizer
or by special blending techniques while the
polymers/resins are in solution or are molten.
Preferably the CO-containing polymer is an ethylene
copolymer, especially a binary or ternary polymer, which
is prepared using carbon monoxide as one of the
monomers. The preparation of such ethylene/carbon
monoxide polymers is known in the art of making ethylene
copolymers. Less preferred are those polymers wherein the carbonyl groups are supplied to the polymer chain by the presence of an alkyl vinyl ketone polymerized into the chain.

The CO-containing polymer usually contains an amount of the >C=O groups (or "CO") along the polymer chain to provide at least 0.2 percent by weight of the total polymer, preferably at least 0.5 percent by weight, and can be as much as 50 percent or more of the total polymer. Below 0.2 percent the effect of the CO-containing polymer is not very likely to provide an appreciably significant effect on the photodegradation of the resin. Above 50 percent, the polymer which contains the CO groups may not exhibit the physical properties needed for attaining the initial strength or other properties desired in the resin article of which it is to be a part. A preferred range is 1 percent to 30 percent by weight, more preferably 2 percent to 20 percent by weight.

The amount of the CO-containing polymer used in the matrix resin usually is an amount in the range of 0.05 percent to 50 percent of the total weight of the formulation. The amount of the anatase TiO₂ used in the matrix resin usually is an amount in the range of 0.05 percent to 25 percent of the total weight of the formulation. Within those ranges, the ratio of the CO-containing polymer to the anatase TiO₂ usually is in the range of 99.9/0.1 to 0.3/99.7, preferably in the range of 99.8/0.2 to 0.5/99.5, most preferably in the range of 99.7/0.3 to 1/99.

In those instances where it is desired to produce articles from resins which contain the rutile
form of TiO₂ as a white pigment and/or opacifier and which sometimes also contain a UV stabilizer or other filler or pigment or opacifier such as SiO₂ and/or CaCO₃ (used, e.g., as an antiblock), one may employ slip agents such as erucylamides or oleamides, or antioxidants or UV stabilizers, such as compounds sold under the following names (some of which are proprietary formulations):

Irganox 1010 --- Tetrakis [methylene 2-(3',5'-di-tert-butyl-4'-hydroxylphenol) propionate] methane,

Irganox 1076 --- Octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate or Octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate,

BHT ---2 ,6-di-t-butyl-p-cresol,

Mark 2047 --- a thiodipropionate ester complex,

Cyasorb UV 531 --- substituted 2-hydroxybenzophenones,

Tinuvin 770 --- hindered piperidines,

Tinuvin 328 --- a benzotriazole, and

Cyasorb UV 5411 --- a benzotriazole.

Some compounds or families of UV stabilizers are, e.g., as follows:

Hindered amines light stabilizers,

Substituted hindered amine light stabilizers,

Hindered piperidines,

Dithiolate metal complexes (e.g. Ni, Co, Cu),

Phosphite esters,

Salicylaldehyde oximes,

Thiobisphenolates,

Hydroxy-benzyl phosphonates,

Substituted 2-hydroxybenzophenones,

2-hydroxyphenyl benztriazoles,

Metal dithiocarbamates,

Metal acetyl acetonates,
Hindered phenols,
Metal dithiophosphate,
Hindered aliphatic amine,
Metal salicylaldehyde oximes,
Peroxydienones,
Thioglycolate 2-hydroxybenzophenones, and
Metal disulfides.

It is within the ambit of the present inventive concept to provide foaming agents, to cause foaming of the matrix resin and produce lightweight articles, and/or add other polymers to the CO-containing polymer/TiO2 compositions, thus preparing an appreciable variety of final products having an enhanced tendency to degrade under the influence of actinic radiation, especially UV.

The following embodiments are for illustration purposes, but the invention is not limited to the particular embodiments illustrated. All parts and percentages are by weight unless otherwise indicated. The expression "LLDPE" is an acronym, widely accepted and recognized in the art, for linear low density polyethylene which is actually an ethylene/1-alkene copolymer prepared by using a coordination catalyst, such as a Ziegler catalyst or the like. The melt flow rate (MFR) of the polymers is measured in accordance with ASTM D-1238 (190/2.16) unless specified otherwise; the MFR is often called melt index (MI) when applied to polyethylene homopolymer.

The following listed ingredients are used in various following examples:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Description of Ingredients</th>
</tr>
</thead>
</table>


<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE-1</td>
<td>Ethylene/octene copolymer, density of 0.941 g/cc and MFR of 40 g/10 min.</td>
</tr>
<tr>
<td>LLDPE-2</td>
<td>Ethylene/octene copolymer, density of 0.920 g/cc and MFR of 10 g/10 min.</td>
</tr>
<tr>
<td>LDPE-1</td>
<td>Branched homopolymer of ethylene, 0.922 g/cc density, MI of 20 g/10 min.</td>
</tr>
<tr>
<td>ECO-1</td>
<td>Copolymer of ethylene/carbon monoxide, containing 1.9 percent CO, MFR 10 g/10 min, density of 0.935 g/cc.</td>
</tr>
<tr>
<td>ECO-2</td>
<td>Copolymer of ethylene/carbon monoxide, containing 10 percent CO, MFR 10 g/10 min.</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium oxide, indicated as the anatase crystal form or the rutile crystal form, or in some instances it can be either one.</td>
</tr>
<tr>
<td>Concentrate #1</td>
<td>Equal parts of ECO-1 and anatase TiO₂, prepared on a Banbury intensive mixer then cooled and ground into small granular pieces.</td>
</tr>
<tr>
<td>Concentrate #2</td>
<td>Equal parts of ECO-2 and anatase TiO₂, prepared on a Banbury intensive mixer then cooled and ground into small granular pieces.</td>
</tr>
<tr>
<td>Concentrate #3</td>
<td>Equal parts of LDPE and rutile TiO₂, prepared on a Banbury intensive mixer then cooled and ground into small granular pieces.</td>
</tr>
</tbody>
</table>
Concentrate #4  Equal parts of LDPE and anatase TiO₂, prepared on a Banbury intensive mixer then cooled and ground into small granular pieces.

Concentrate #5  Equal parts of ECO-2 and rutile TiO₂, prepared on a Banbury intensive mixer then cooled and ground into small granular pieces.

Concentrate #6  Equal parts of ECO-1 and rutile TiO₂, prepared on a Banbury intensive mixer then cooled and ground into small granular pieces.

Example 1:

A composite blend is prepared by blending 9.9 parts of LLDPE-1, 0.3 parts of LLDPE-2, and 4.8 parts of Concentrate #1. The components are tumble dry blended prior to being fabricated into cast film at 550°F (288°C) of 1.2 mil (30 micrometers) thickness. Strips of film, 1-inch by 8-inch (2.5 cm by 20 cm) are cut from the cast film and subjected to outside weathering in accordance with ASTM D-1435-85. By analyses of the parameters of interest, average tensile, average yield and percent elongation at break are determined and analyzed in accordance with ASTM D-882. The brittle point is determined to be that point where the tensile at break and yield strength values were identical and the film samples demonstrated brittleness when handled. The data for the outside weathering are shown in TABLE I.

Example 2:
In similar manner to Example 1, a composite blend is prepared consisting of 9.9 parts of LLDPE-1, 0.3 parts of LLDPE-2, and 4.8 parts of Concentrate #2. The composite is tested by outside weathering and the data are shown in Table I.

Example 3-6:

In similar manner to the foregoing descriptions and examples, other tests are made using various combinations to make composites, holding the LLDPE-1 and LLDPE-2 content constant, using different concentrates (some of which are not examples of the invention, but are for comparison purposes to illustrate the synergism of the ECO/anatase TiO2 combination) are shown in Table I.
Table I

<table>
<thead>
<tr>
<th>Example</th>
<th>Concentrate</th>
<th>% Elongation/Elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1 (Comp.)</td>
<td>497/ductile</td>
</tr>
<tr>
<td></td>
<td>2 (Comp.)</td>
<td>456/ductile</td>
</tr>
<tr>
<td></td>
<td>3*</td>
<td>447/ductile</td>
</tr>
<tr>
<td>10</td>
<td>4*</td>
<td>412/ductile</td>
</tr>
<tr>
<td>5*</td>
<td>5*</td>
<td>505/ductile</td>
</tr>
<tr>
<td>6*</td>
<td>6</td>
<td>445/ductile</td>
</tr>
</tbody>
</table>

*Example not of the invention, but for comparison

The data in Table I indicate that the synergistic mixture of ECO/anatase TiO₂ (concentrates #1 & #2) causes a very rapid embrittlement of the LLDPE film in only 17 days of exposure, a remarkable amount of embrittlement when compared to the other examples which were tested in the same manner. The comparison examples which retained a high degree of elongation/elasticity (i.e. they remained ductile) indicated that the use of rutile alone, or rutile/ECO combinations, or anatase/LDPE combinations had no noticeable effect on embrittlement during the 17 day test.

The following are preferred ranges and ratios for the practice of the above embodiments:

For the ratio of ECO/anatase TiO₂ in the concentrate, the range of 1/99 to 99/1 is believed to be operable, preferably 40/60 to 90/10, most preferably 50/50 to 80/20.
Example 9 Heat Seal Range Compared With Prior Art

Hot tack tests are performed on a "Pack Forsk" instrument which is fully automated and is equipped with an Instron type seal strength testing device. The dwell time is set at 0.5 seconds. The delay time (between the formation of seal and the strength) is set at 0.2 seconds. The film samples are 1-inch (2.5 cm) wide strips of uniform thickness. Each data point is calculated from an average of at least 3 measurements.

The tear resistance is measured by Elmendorf tear test type B, which is ASTM # D-1922. Each data point is an average of four measurements.

Films from which testing samples are taken are prepared by dry blending the components for 1 hour and then extruding the well-mixed ingredients through a 1-inch (2.5 cm) 24/1 L/D MPM extruder and fabricated into cast film (film gauge of 2.5 to 2.7 mils, i.e. about 63 to 69 micrometers, under the following conditions:

<table>
<thead>
<tr>
<th>Extruder Location</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>370°F/188°C</td>
</tr>
<tr>
<td>Zone 2</td>
<td>430°F/221°C</td>
</tr>
<tr>
<td>Zone 3</td>
<td>450°F/232°C</td>
</tr>
<tr>
<td>Gate</td>
<td>450°F/232°C</td>
</tr>
<tr>
<td>Adapter</td>
<td>450°F/232°C</td>
</tr>
<tr>
<td>Feed Block</td>
<td>450°F/232°C</td>
</tr>
<tr>
<td>90° Adapter</td>
<td>450°F/232°C</td>
</tr>
<tr>
<td>Die #1</td>
<td>450°F/232°C</td>
</tr>
<tr>
<td>Die #2</td>
<td>450°F/232°C</td>
</tr>
<tr>
<td>Chill Roll</td>
<td>59°F/15°C</td>
</tr>
</tbody>
</table>
A typical prior art composite contains about 73 percent LLDPE, about 25 percent LDPE, and about 2 percent TiO₂. The heat seal temperature range and the tear strength of this currently used composite, when fabricated into a cast film without the TiO₂, are 225°F to 275°F (107°C to 135°C) and 200 grams, respectively. With the TiO₂ added to the LDPE/LLDPE formulation, the heat seal temperature range and tear strength become reduced to 230°F to 265°F (110°C to 129°C) and 146 grams, respectively.

When an ethylene/carbon monoxide (ECO) copolymer is used with the LLDPE in place of the LDPE, and without the TiO₂, the heat seal temperature range and tear resistance is 225°F to 280°F and 592 grams, respectively. Then when TiO₂ is added to the LLDPE/ECO blend, the heat seal temperature and tear strength is 235°F to 295°F and 606 grams, respectively. We believe that an acid-base interaction between TiO₂ (acidic surface) and ECO (basic carbonyl) contributes to better dispersion of TiO₂ in the polymer matrix which is essentially non-polar. For this heat seal effect the TiO₂ can be either anatase or rutile or any variety having an acid surface. Other particulate solid compounds having acid surfaces may be employed in place of, or along with, the TiO₂ and the CO-containing olefin polymer.

Example 10

The use of ECO/TiO₂ in place of LDPE/TiO₂ is found to result in widening the heat seal temperature range of a wide variety of polymers into which the ECO/TiO₂ is incorporated, especially olefin polymers and copolymers such as LLDPE, HDPE, and LDPE and the like.
The benefits of the ECO/TiO₂ additives are found in blown films as well as cast films.

For the purposes of improving the heat seal range of the preferred LLDPE the following amounts are preferred:

<table>
<thead>
<tr>
<th>Component*</th>
<th>Operative wt. %</th>
<th>Preferred wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>20 to 99</td>
<td>30 to 95</td>
</tr>
<tr>
<td>ECO</td>
<td>0.5 to 60</td>
<td>1.0 to 30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1 to 30</td>
<td>1 to 20</td>
</tr>
</tbody>
</table>

*The ECO copolymer usually contains 1 to 50 weight percent CO. The LLDPE usually contain any one or more alkene comonomers in the C₃–C₁₀ range.
1. A photodegrading agent comprising a blend of anatase TiO\(_2\) and at least one photodegrading polymer containing carbonyl groups along the polymer chain.

2. An agent as claimed in Claim 1, wherein said polymer is prepared by copolymerizing an amount of carbon monoxide with a greater amount of olefin monomer.

3. An agent as claimed in Claim 1 or Claim 2, wherein said polymer is an ethylene copolymer.

4. An agent as claimed in any one of the preceding claims, wherein said polymer comprises from 0.5 percent up to 50 percent by weight of CO.

5. An agent as claimed in any one of the preceding claims, wherein the weight ratio of said polymers to anatase TiO\(_2\) is 99.8:0.2 to 0.5:99.5.

6. An Agent as claimed in any one of the preceding claims, comprising rutile TiO\(_2\) and/or a UV stabilizer to exhibit a predetermined regulated rate of photodegradation.

7. A photodegradable composition comprising a polymeric matrix containing anatase TiO\(_2\) and at least
one photodegrading polymer containing carbonyl groups along the polymer chain.

8. A composition as claimed in Claim 7, wherein said CO-containing polymer is as defined in any one of Claims 2 to 4 and/or the ratio of said CO-containing polymer to anatase TiO₂ is as defined in Claim 5.

9. A composition as claimed in Claim 7 or Claim 8, wherein said matrix material comprises a polyolefin, polyester, polyurethane, polyamide, polyepoxide, polyacrylate, or polycarbonate.

10. A composition as claimed in Claim 7 or Claim 8, wherein said matrix material comprises an ethylene, styrene, propylene, or butene polymer or copolymer.

11. A composition as claimed in Claim 10, wherein said matrix material comprises LDPE, HDPE, MDPE, or LLDPE.

12. A composition as claimed in any one of Claims 7 to 11, comprising rutile TiO₂, and/or a UV stabilizer to regulate the rate of photodegradation.

13. A process of synergistically enhancing the photodegradation rate of photodegradation polymers containing carbonyl groups along the polymer chain, the said process comprising incorporating the anatase form of TiO₂ therein.

14. A process of accelerating the photodegradation rate of a polymeric matrix material, said process comprising incorporating into said
matrix material a photodegrading agent as claimed in any one of Claims 1 to 6.

15. A process of providing a regulated rate of photodegradation to a polymeric matrix material,
said process comprising blending said matrix material with anatase TiO₂, at least one photodegradation polymer containing carbonyl groups along the polymer chain and optionally rutile TiO₂ and/or a UV stabilizer.

16. A method for broadening the heat seal range of a heat sealable polymeric matrix material,
said method comprising incorporating into said matrix material an amount of a mixture of TiO₂ and a polymer containing carbonyl groups along the polymer chain effective in broadening the heat-seal range.

17. A composition as claimed in Claim 11 wherein said matrix material comprises HDPE.

18. Use of the composition of Claim 17 in preparing molded articles.

19. A composition as claimed in Claim 11 wherein said matrix material comprises LLDPE or LDPE.


21. A composition as claimed in Claim 10 wherein said matrix material comprises a styrenic polymer or copolymer.

22. Use of the composition of Claim 21 in preparing a foam.
# INTERNATIONAL SEARCH REPORT

**INTERNATIONAL APPLICATION NO.** PCT/US89/05749

## I. CLASSIFICATION OF SUBJECT MATTER

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

| IPC(5) | US 524/612; 523/125,124 |

## II. FIELDS SEARCHED

<table>
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<th>Classification System</th>
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<td>U.S.</td>
<td>524/612; 523/125</td>
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

## III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
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<tbody>
<tr>
<td>Y</td>
<td>US, A, 3,676,401 (HENRY) 11 July 1972, Column 2,3,4</td>
<td>1-12, 13-22</td>
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<td>Y</td>
<td>US, A, 3,860,538 (GUILLET) 14 January 1975, Entire document</td>
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<td>A</td>
<td>US, A, 3,981,856 (HUDGIN) 21 September 1976, Columns 1-4</td>
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</table>

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  * A - document defining the general state of the art which is not considered to be of particular relevance
  * E - earlier document published on or after the international filing date
  * L - document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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* X - document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

* Y - document of particular relevance; the claimed invention cannot be considered novel but the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* A - document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search: 27 FEBRUARY 1990

Date of Mailing of this International Search Report: 28 MAR 1990

International Searching Authority: ISA/US

Signature of Authorized Officer: [Signature]