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(21) International Application Number: PCT/US97/14926 (22) International Filing Date: 25 August 1997 (25.08.97) (30) Priority Data: 08/841,062 29 April 1997 (29.04.97) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: OLSON, David, B.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). BURNS, David, M.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: JORDAN, Robert, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: BOUND ULTRAVIOLET LIGHT ABSORBERS (57) Abstract Oligomeric materials contain ultraviolet light absorbing compounds that are covalently bound to the oligomer backbone through an ester or amide linkage. These ultraviolet light absorbing oligomers may be combined with polymers such as polyolefins to provide protection against the harmful effects of ultraviolet light.		

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BOUND ULTRAVIOLET LIGHT ABSORBERS

Field of the Invention

This invention relates to oligomers that contain ultraviolet light
5 absorbing compounds (UVAs) covalently bound to the oligomeric backbone. The
invention also relates to stabilization of polymers or other substrates against
photochemical degradation by use of the oligomers.

Background of the Invention

10 Many plastics tend to degrade when exposed to sunlight or other
sources of ultraviolet (UV) light. This exposure results in, for example, loss of
tensile strength, embrittlement, and discoloration. To help prevent such
degradation, ultraviolet light stabilizers are often incorporated into a polymer
composition, which is used as a protective top layer for underlying materials. These
15 uv light stabilizers perform well but are often not stable in or compatible with the
polymer, which results in the stabilizer leaving the polymer by leaching, migration,
vaporization, or other means. When the uv stabilizer levels are lowered in this
manner, their protective effect is diminished, leading to degradation of the polymer
and the underlying materials.

20 Molecules that function as ultraviolet light absorbers are generally known in
the art. For example, in U.S. Patent No. 4,853,471 Rody et al. describe 2-(2-
hydroxyphenyl)-benzotriazole compounds that are useful as ultraviolet light
absorbers. These compounds are described as useful in the stabilization of a wide
variety of polymeric materials against ultraviolet light, particularly those that are
25 used in the preparation of photographic materials. Other classes of ultraviolet light
absorbers include the 2-hydroxybenzophenones and the diphenylcyanoacrylates.

While such compounds are known to absorb ultraviolet light, their
incompatibility with the polyolefins often used as the top film in multilayer sheetings
has limited their usefulness in such constructions. The low solubility and high
30 mobility of typical ultraviolet light absorbers in polyolefins results in an inability to
maintain high levels of these compounds in polyolefin films; the compounds tend to
bloom or migrate out of the film, and the protective properties of the compounds
are lost.

Much effort has been directed to the development of methods of
35 maintaining the uv stabilizer compound in a selected polymeric matrix. Ultraviolet
light stabilizers have been developed that have polymerizable functionalities. The

polymerizable stabilizer is then incorporated into the polymer as a co-monomer or copolymerized with another monomer to form a stabilizing polymer that can be added to the desired polymer. Because the stabilizing compound is then part of the polymer backbone, it remains in the polymer composition and the stabilizing

5 benefits are retained for a longer period of time. Examples of incorporation of a stabilizing monomer into a polymer backbone may be found in, for example, Vogl et al., POLYMER, Vol. 26, p. 1288 (1985); U.S. Pat. Nos. 3,313,866 (Horton et al.), 4,128,536 (Brodsky et al.), and 4,528,311 (Beard et al.).

There has also been development in the area of "attaching" the

10 ultraviolet light absorbing compound to a polymer backbone by selecting UV light absorbers with groups that react with various functionalities present on the polymer. Fu et al., in U.S. Patent No. 4,413,096, describe α -olefin copolymers wherein hindered amine light stabilizers are pendant to the polymer backbone. The Fu copolymers may be prepared by transesterification of the polymer with the hindered

15 amine light stabilizing compound.

There is a continuing need in the art for a method of stabilizing polymers such as polyolefins with ultraviolet light absorbing compounds that provides lasting protection both to the polyolefin and to articles that incorporate the polyolefin.

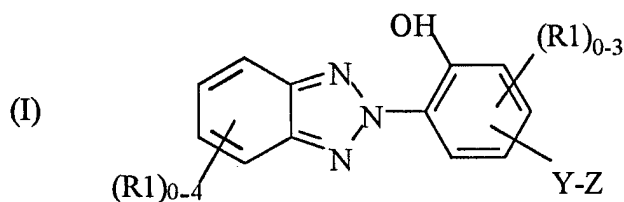
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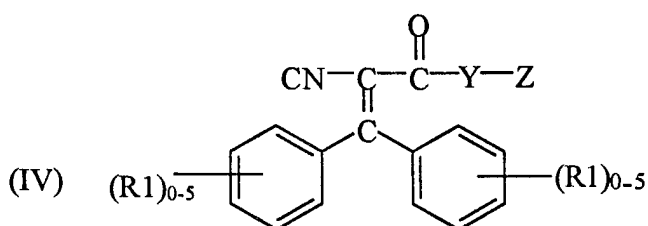
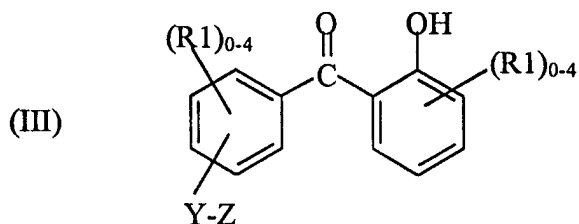
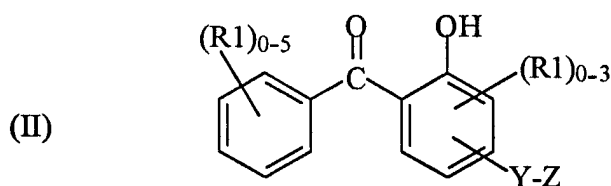
Summary of the Invention

We have found that hydroxy or amine functional ultraviolet light absorbing compounds may be covalently bound to a carboxyl functional oligomer. This covalent bonding allows us to deliver a compatible non-fugitive uv absorber to

25 polyolefin type polymers. Accordingly, the invention provides an ultraviolet light absorbing oligomer made up of an ultraviolet light absorbing oligomer comprising the reaction product of a carboxyl functional oligomer and a hydroxy or amine functional ultraviolet light absorbing compound, wherein the ultraviolet light absorbing compound is a group of formula (I), (II), (III), or (IV):

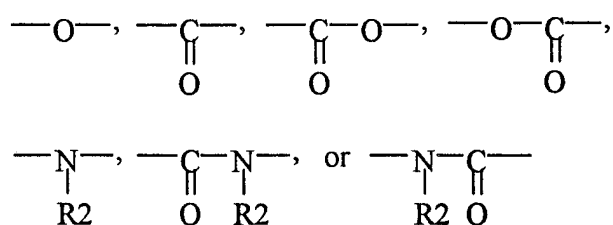
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wherein each R1 is independently halogen, hydroxy, straight-chain or branched C₁₋₁₂ alkyl, straight-chain or branched C₂₋₁₂ alkenyl, straight-chain or branched C₁₋₁₂ alkoxy, straight-chain or branched C₂₋₁₂ alkenyloxy, straight-chain or branched C₁₋₁₂ alkanol, amino, straight-chain or branched C₁₋₁₂ alkylamino, or straight-chain or
 10 branched C₁₋₁₂ dialkylamino; Y is a C₁₋₁₈ alkylene or C₂₋₁₈ alkenylene group which may be straight-chain or branched and which may be interrupted by one or more



wherein each R2 is independently H or C₁₋₆ alkyl that may be straight-chain or branched; and Z is -OH or -NH₂.

The invention also provides polymer compositions that contain the UV light absorbing oligomer and a polyolefin, and articles such as retroreflective sheetings, conformable pavement markers, and signs that contain films made of the polymer composition.

5 In one such aspect the invention provides a conformable marking sheet comprising a top polymeric film layer having glass microspheres and skid resistant particles partially embedded therein, the film comprising a polyolefin and the ultraviolet light absorbing oligomer of the invention; a base layer comprising a deformable thermoplastic polymer and a nonreinforcing mineral particulate; a
10 pressure sensitive adhesive layer; and a release liner.

 In another aspect of the invention is provided an enclosed-lens retroreflective sheeting comprising a layer of lenses anchored in a binder layer, a specularly reflective layer underlying the lenses, and a top layer comprising a polymeric film, said film comprising a polyolefin and the ultraviolet light absorbing
15 oligomer of the invention.

 All percentages are weight percentages based on total composition weight unless otherwise specified.

Detailed Description of the Invention

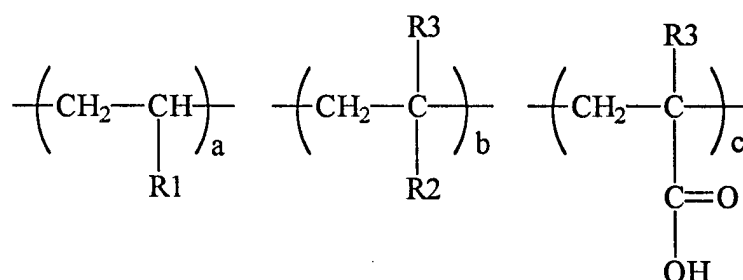
20 The UV light absorbing oligomers of the invention are generally prepared by reacting a carboxyl bearing oligomer with a hydroxy or amine functional ultraviolet light absorbing compound. The carboxyl functional oligomer contains at least one monomer having a pendant carboxyl (-COOH) group. Carboxyl functional oligomers useful in the formation of the UV light absorbing
25 oligomers of the invention typically have a weight average molecular weight of about 100 to 10,000, preferably about 1000 to 3500. The acid number (mg KOH required to neutralize 1 gram of the oligomer) of the oligomer is generally about 40 to 180.

 Monomers useful in the formation of the carboxyl functional
30 oligomer include ethylenically unsaturated carboxylic acids. The carboxyl functional oligomer may be a homopolymer or copolymer of such carboxy bearing monomers. The copolymer may contain different carboxy bearing monomers, or may contain a carboxy bearing monomer and a non-carboxy bearing monomer. Examples of useful types of non-carboxy bearing monomers include ethylenically
35 unsaturated carboxylic acid esters, olefins, vinyl compounds, and the like.

Suitable ethylenically unsaturated carboxylic acids include alkenoic and aralkenoic mono- di- and tri- carboxylic acids having up to 20 carbon atoms as well as acids having higher numbers of carboxyl groups. Examples of such acids include acrylic acid, methacrylic acid, fumaric acid, maleic acid, crotonic acid, itaconic acid and cinnamic acid. Of these, acrylic acid and methacrylic acid are preferred.

Comonomers that may be used in the preparation of the carboxyl functional polymer include olefins such as ethylene, propylene, and butylene; ethylenically unsaturated aromatic monomers that contain up to 20 carbon atoms such as styrene and vinyl tolulene; ethylenically unsaturated esters of carboxylic acids that contain a total of up to 20 carbon atoms such as vinyl acetate; and the like. Of these, the olefins are a preferred class of comonomer, and ethylene is particularly preferred.

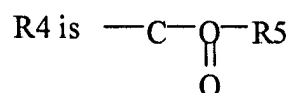
The carboxyl functional oligomer may be an oligomer having
15 randomly recurring structural units of the formula (V):



(V)

20

wherein R3 is H or C₁₋₁₈ alkyl which may be straight or branched;



each R5 is independently H or C₁₋₆ alkyl which may be straight or branched;
25 and a, b, and c are selected to provide a weight average molecular weight of about 100 to 10,000, provided that c is at least one.

Ethylene-acrylic acid copolymer having a weight average molecular weight of about 1000 to 3500 is a particularly preferred carboxyl functional oligomer. Commercially available examples of preferred ethylene-acrylic acid

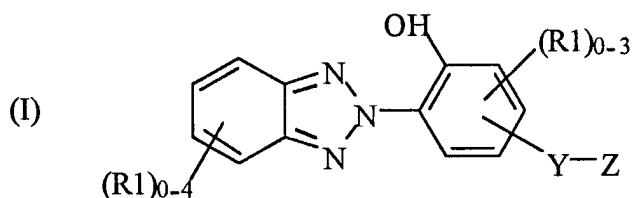
copolymers include the A-C® copolymers available from Allied Signal Inc., Morristown, NJ.

The carboxyl functional oligomer can be prepared using polymerization methods known in the art. See, for example, Knutson et al., U.S.

- 5 Pat. No. 3,658,741, which is incorporated herein by reference. Detailed information on polymer and oligomer preparation may be found, for example, in the Encyclopedia of Polymer Science and Engineering, Vol. 6, Wiley & Sons 1986, pp. 383-429.

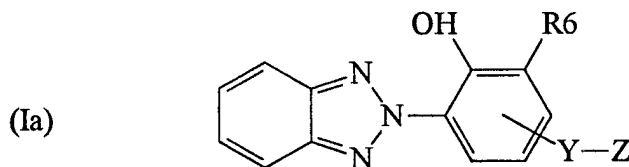
- The carboxyl functional oligomer is reacted with one or more
 10 hydroxy or amine functional ultraviolet light absorbing compounds to produce the UV light absorbing oligomer of the invention. In addition to absorbing ultraviolet light, the ultraviolet light absorbing compounds useful in the invention are preferably transparent to visible light. Useful classes of hydroxy and amine functional ultraviolet light absorbing compounds include hydroxy and amine
 15 containing 2-hydroxyphenylbenzotriazoles, 2-hydroxybenzophenones, and diphenylcyanoacrylates.

- Any 2-hydroxyphenylbenzotriazole ultraviolet light absorbing compound that contains a terminal hydroxy or amine group may be used in the material of the invention. Suitable 2-hydroxyphenylbenzotriazole compounds
 20 include those having formula (I):



- wherein each R1 is independently halogen, hydroxy, straight-chain or branched C₁₋₁₂ alkyl or C₂₋₁₂ alkenyl, straight-chain or branched C₁₋₁₂ alkoxy, straight-chain or branched C₂₋₁₂ alkenyloxy, straight-chain or branched C₁₋₁₂ alkanol, amino, straight-
 25 chain or branched C₁₋₁₂ alkylamino, or straight-chain or branched C₁₋₁₂ dialkylamino; Y is a C₁₋₁₂ alkylene or C₂₋₁₂ alkenylene group that may be straight or branched and that may be interrupted by one or more -O-, -C(O)-, -C(O)O-, -OC(O)-, -NR₂-, -C(O)NR₂-, or -NR₂C(O) groups; and Z is OH or NH₂; and R₂ is H or C₁₋₆ alkyl which may be straight or branched;

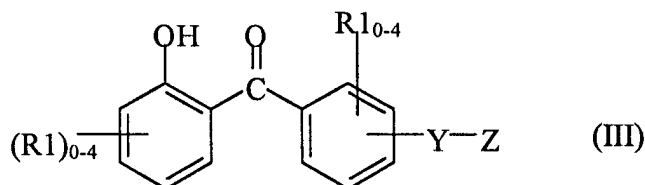
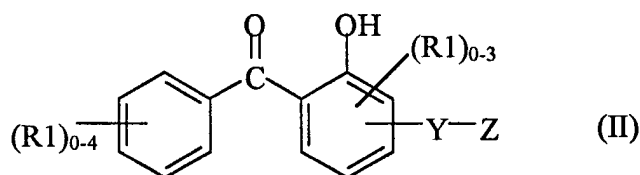
Of these, 2-hydroxyphenylbenzotriazole compounds having formula (Ia) are preferred:



5 wherein R6 is H or C₁₋₄ alkyl which may be straight or branched.

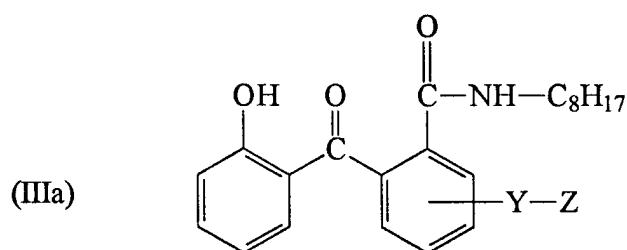
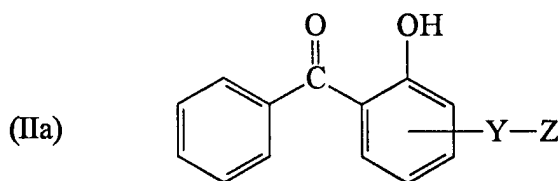
Another useful class of ultraviolet light absorbing compounds is the 2-hydroxybenzophenones. So long as they contain a terminal hydroxy or amine group, any 2-hydroxybenzophenone ultraviolet light absorbing compound may be used. Examples of 2-hydroxybenzophenone compounds that may be used in the

10 invention include those of formula (II) and (III):



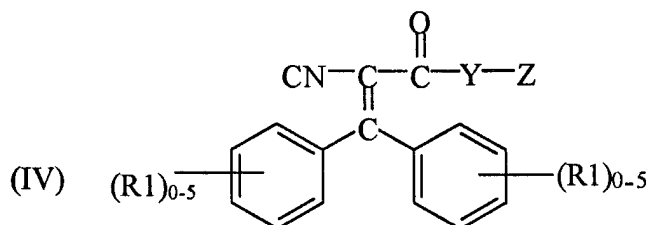
wherein each R1 is independently halogen, hydroxy, straight-chain or branched C₁₋₁₂ alkyl, straight-chain or branched C₂₋₁₂ alkenyl, straight-chain or branched C₁₋₁₂ alkoxy, straight-chain or branched C₂₋₁₂ alkenyloxy, straight-chain or branched C₁₋₁₂ alkanol, amino, straight-chain or branched C₁₋₁₂ alkylamino, or straight-chain or branched C₁₋₁₂ dialkylamino; Z is OH or NH₂; and Y is a C₁₋₁₂ alkylene or alkenylene group that may be straight-chain or branched and that may be interrupted by one or more -O-, -C(O)-, -C(O)O-, -OC(O)-, -NR₂-, -C(O)NR₂-, or -NR₂C(O) groups wherein R₂ is H or C₁₋₆ alkyl that may be straight-chain or branched.

Examples of particular 2-hydroxybenzophenone compounds useful in the invention include compounds of formulas (IIa) or (IIIa):



- 5 wherein the octyl group may be straight-chain or branched.

Diphenylcyanoacrylate ultraviolet light absorbing compounds may also be used, so long as they contain a terminal hydroxy or amine group. Examples of useful diphenylcyanoacrylate compounds include those of formula (IV):



10

- wherein each R1 is independently halogen, hydroxy, straight-chain or branched C₁₋₁₂ alkyl, straight-chain or branched C₁₋₁₂ alkenyl, straight-chain or branched C₁₋₁₂ alkoxy, straight-chain or branched C₁₋₁₂ alkenyloxy, straight-chain or branched C₁₋₁₂ alkanol, amino, straight-chain or branched C₁₋₁₂ alkylamino, or straight-chain or
- 15 branched C₁₋₁₂ dialkylamino; Z is OH or NH₂; and Y is a C₁₋₁₂ alkylene or alkenylene group that may be straight or branched and that may be interrupted by one or more -O-, -C(O)-, -C(O)O-, -OC(O)-, -NR₂-, -C(O)NR₂-, or -NR₂C(O) groups; and R₂ is H or C₁₋₆ alkyl which may be straight-chain or branched.

Dimers of any of these ultraviolet light absorbing compounds can be used as well.

Other ultraviolet light absorbing compounds may also be used, provided they contain a terminal hydroxy or amine group. Examples of such compounds include p-hydroxybenzoates and triazines. The hydroxy or amine functional ultraviolet light containing compounds may be used alone or in combination in the oligomers, materials and films of the invention.

The UV light absorbing oligomers of the invention are prepared by reacting the carboxyl functional oligomer with the hydroxy or amine functional ultraviolet light absorbing compound. No solvent is necessary, as the reaction may be carried out in the molten or liquid oligomer, but an organic solvent may be used if desired.

In general the reaction is carried out by combining the carboxyl functional oligomer, the hydroxy or amide functional UV light absorbing compound and an appropriate catalyst in a reaction vessel. The mixture is heated with stirring until the oligomer melts. Stirring at an elevated temperature, e.g. 220-240°C may be continued until no unreacted UVA remains. The reaction mixture is monitored by TLC (Thin Layer Chromatography) or other suitable means until the reaction is determined to be complete.

The carboxyl functional oligomer and the hydroxy or amine functional UV light absorbing compound are present in proportions selected to provide the desired amount of UV light absorber loading in the oligomer. Levels of about 2 to 25 wt-% based on the total oligomer weight are preferred, although higher or lower levels may be used depending on the particular end use.

The reaction is carried out in the presence of an effective esterification catalyst, such as dibutyl tin oxide, dibutyl tin hydroxide, butyl tin oxide hydroxide, stannous octoate, lithium ricinoleate and bismuth neodecanoate. The preferred catalyst is butyl tin oxide hydroxide (available as FASTCAT 4100 from Atochem North America, Inc., Philadelphia, PA). The catalyst generally makes up about 0.01 to 5.0 wt-% of the reaction mixture, preferably about 0.1 to 1.0 wt-%, although slightly more or less may be required depending on the particular catalyst employed.

The ultraviolet light absorbing oligomer thus formed may be used as is or blended into polymers such as polyolefins which may be further processed as desired. For example, they may be formed into films that are durable and provide

protection to underlying substrates or materials against the harmful effects of ultraviolet light.

The polymeric material of the invention is made by combining the ultraviolet light absorbing oligomer of the invention with a polymer such as a polyolefin. Because it is covalently bound to the oligomer, the ultraviolet light absorber does not bloom or migrate out of the polymer, thereby increasing the useful life of articles that are constructed using films made of the material.

Polyolefins that may be used in the polymeric material of the invention include polymers that are made from at least one olefinic monomer. Examples of such olefinic monomers include ethylene, propylene, butylene, styrene, and the like, with ethylene the preferred olefinic monomer.

The polyolefin may be a homopolymer of the olefinic monomer, or it may be a copolymer of different olefinic monomers or of an olefinic monomer and another monomer. The comonomer may be any monomer that can be co-polymerized with the olefinic monomer, so long as it does not result in incompatibility with the UV light absorbing oligomer. Useful types of comonomers include ethylenically unsaturated carboxylic acids; ethylenically unsaturated carboxylic acid esters; and vinyl containing monomers. The ethylenically unsaturated carboxylic acids are a preferred class of comonomers, with acrylic acid especially preferred.

The polymeric material is prepared by combining the UV light absorbing oligomer of the invention with a polyolefin. The UV light absorbing oligomer is generally present in an amount high enough to provide protection from ultraviolet light, but not so high that the material migrates, separates, or blooms out of the polyolefin. Typically the polymeric material contains a sufficient amount of the UV light absorbing oligomer to provide about 0.05 to 50 wt-%, preferably about 1 to 20 wt-% of the ultraviolet light absorbing compound in the material based on the total material weight.

The polymeric material may be prepared by blending a melt of the polyolefin with a melt of the UV light absorbing oligomer with stirring until the mixture is uniform. After uniformity is achieved, the mixture may be pressed or formed into a film or other shape using methods known in the art. The film may also be prepared by co-extruding the polyolefin polymer and the UV light absorbing oligomer directly into a film.

Films containing the polymeric material of the invention may be used as the top layer or cover film of a multilayered retroreflective sheeting.

Retroreflective sheetings are generally known in the art, as seen for example in Bailey et al., U.S. Patent No. 4,767,659, which is incorporated herein by reference. The polymeric films provide protection to the lower layers of the sheeting from ultraviolet light, thereby extending the useful life of the sheeting and articles that
5 incorporate the sheeting.

In addition to providing protection from ultraviolet light, when used as the top layer of a retroreflective sheeting, the polymeric film should be sufficiently extensible to withstand substantial stretching such as the embossing of a license plate, sufficiently soft that it resists localized delamination when stretched to
10 conform to an irregular surface, and should have good impact resistance. Preferably, when used as the top layer of a retroreflective sheeting the polymeric film has an elongation of at least about 100%, good impact resistance, toughness, and transparency.

Retroreflective sheetings that contain the polymeric film of the invention as a top layer typically contain multiple layers. One example of a suitable
15 retroreflective sheeting is a sheeting article that contains a binder layer; a layer of glass microspheres fully or partially embedded in the binder layer; a specularly reflective layer; and an adhesive layer covered by a removable liner. Other layers may be present as desired.

To prepare a retroreflective sheeting using the polymeric film of the invention, the film is laminated to a retroreflecting base material that contains
20 multiple layers as described above.

The retroreflective sheetings prepared using the polymeric film of the invention may be applied to a wide variety of articles, including traffic signs,
25 barriers, and cones, as well as embossed license or information plates. The preparation of embossed information plates is described in U.S. Patent Nos. 5,085,918 and 5,227,194, both of which are incorporated herein by reference.

The films of the invention may also be used in the preparation of conformable pavement marking sheets. Such conformable marking sheets are
30 described in Lasch et al., U.S. Patent No. 5,194,113, which is incorporated herein by reference.

When used in the preparation of a conformable marking sheet, the polymeric film should be sufficiently ductile to allow the sheet to conform to the surface of the pavement or other substrate in order to improve the adhesion of the
35 sheet to the substrate. When used as a top layer in a conformable marking sheet,

the polymeric film preferably includes a visibility enhancing pigment such as titanium dioxide or lead chromate.

The polymeric film top sheet or layer may be extruded or laminated directly onto the other layers of the conformable sheet, or an adhesive or other layer
5 may be interposed between the top layer and other layers of the sheet.

The polymeric films of the invention may also be used as a marking sheet independent of a conforming layer. If used in this manner, the polymeric film may be laminated to a layer of pressure sensitive adhesive to improve adhesion to the pavement or other substrate. A release liner may also be present to provide ease
10 of handling and storage. In addition, particles may be fully or partially embedded in the top surface of the film to improve the retroreflectivity and/or skid resistance properties of the film.

The invention is further described by reference to the following examples, which are understood to be illustrative only and not limiting of the
15 invention.

Examples

Example 1

20 This example utilized Allied-Signal A-C 5120 oligomer, a copolymer of about 15% acrylic acid and 85% ethylene, having a weight average molecular weight of about 1500 and a carboxylic acid equivalent weight of about 475 and Uvinul® X-19, 2-hydroxy-4-(2-hydroxyethoxy) benzophenone, available from BASF Inc., Ludwigshafen, Germany.

25 To prepare the ultraviolet light absorbing oligomer, 25 g of A-C 5120 was placed in a 100 ml, 3-necked round bottom flask. Ten grams of the Uvinul® X-19 and 0.008 g of Fastcat® 4100 butyl tin hydroxide catalyst were added, without use of a solvent. The reaction mixture was stirred and heated to 150°C, when a homogeneous melt was formed. A nitrogen sparge was added
30 beneath the liquid level, heating was continued until the temperature reached 220°C, and the mixture was held at 220-230°C, with stirring, for 4 hours. After 4 hours TLC (50% ethyl acetate/50% hexanes) showed little unreacted benzophenone. The molten mixture was poured from the flask into an aluminum pan and allowed to cool to room temperature.

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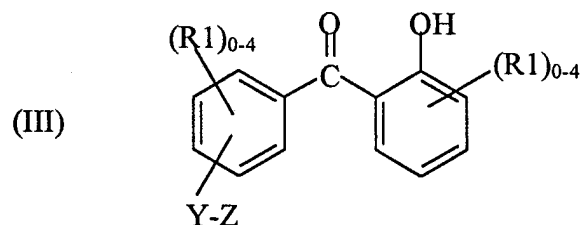
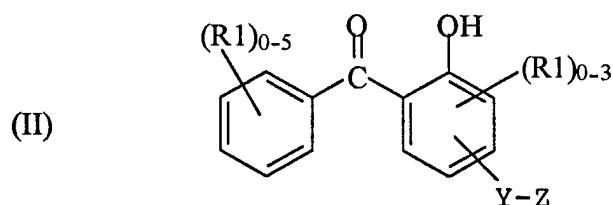
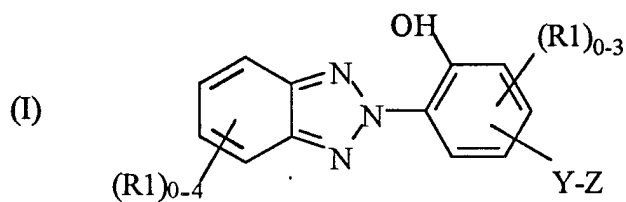
Example 2

Twenty-five grams of the product of Example 1 in pulverized form was dry blended with 490 g of Primacor[®] 3440 (polyethylene-co-acrylic acid), available from Dow Chemical, Midland, MI). The blend was extruded onto a polyester carrier as a nominal 2 mil (51 microns) film, and the temperature profile was Zone 1 - 350°F (177°C), Zone 2 - 380°F (193°C), Zone 3 and die - 420°F (216°C). Melt temperature was 306°F (152°C). Extrusion took place on a Haake 3/4" single screw extruder. The UVA loading of the film was 1.2 wt-%.

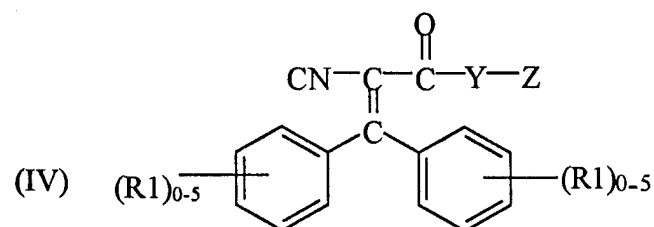
The above specification, examples and data provide a complete description of the manufacture and use of the composition of the invention. Since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended.

WE CLAIM:

1. An ultraviolet light absorbing oligomer comprising the reaction product of a carboxyl functional oligomer and a hydroxy or amine functional ultraviolet light absorbing compound, wherein the ultraviolet light absorbing
- 5 compound is a group of formula (I), (II), (III), or (IV):



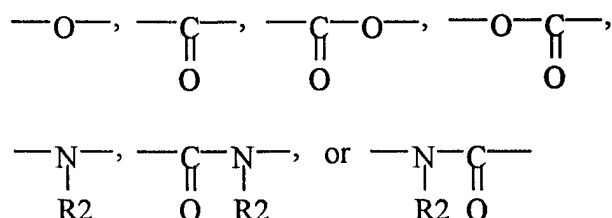
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wherein each R1 is independently halogen, hydroxy, straight-chain or branched C₁₋₁₂

15 alkyl, straight-chain or branched C₂₋₁₂ alkenyl, straight-chain or branched C₁₋₁₂

alkoxy, straight-chain or branched C₂₋₁₂ alkenyloxy, straight-chain or branched C₁₋₁₂ alkanol, amino, straight-chain or branched C₁₋₁₂ alkylamino, or straight-chain or branched C₁₋₁₂ dialkylamino; Y is a C₁₋₁₈ alkylene or C₂₋₁₈ alkenylene group which may be straight-chain or branched and which may be interrupted by one or more



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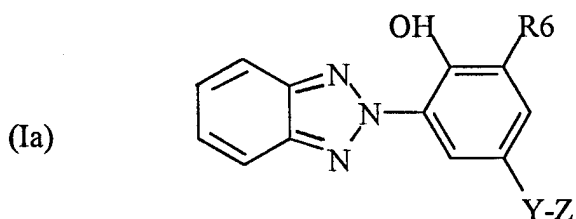
wherein each R₂ is independently H or C₁₋₆ alkyl that may be straight-chain or branched; and Z is -OH or -NH₂.

2. The ultraviolet light absorbing oligomer of claim 1 wherein the group of formula (I), (II), (III), or (IV) comprises about 1 to 25 wt-% of the oligomer.

3. The ultraviolet light absorbing oligomer of claim 1 wherein at least one ultraviolet light absorbing compound is a group of formula (I).

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4. The ultraviolet light absorbing oligomer of claim 1 wherein at least one ultraviolet light absorbing compound is a group of formula (Ia):

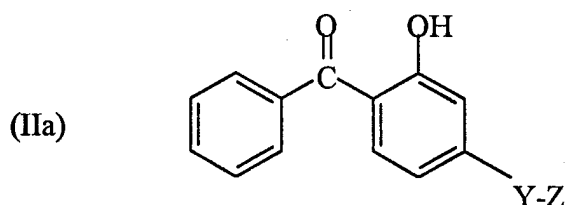


20 wherein R₆ is H or C₁₋₄ alkyl which may be straight or branched.

5. The ultraviolet light absorbing oligomer of claim 1 wherein at least one ultraviolet light absorbing compound is a group of formula (II).

6. The ultraviolet light absorbing oligomer of claim 1 wherein at least one ultraviolet light absorbing compound is a group of formula (III).

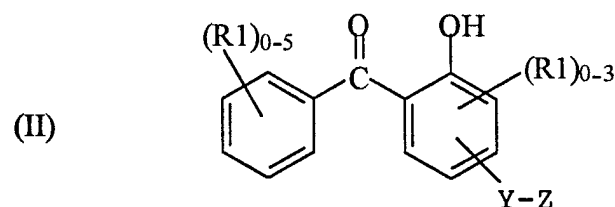
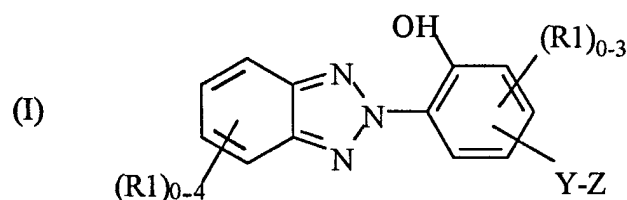
7. The ultraviolet light absorbing oligomer of claim 1 wherein at least one ultraviolet light absorbing compound is a group of formula (IIa):

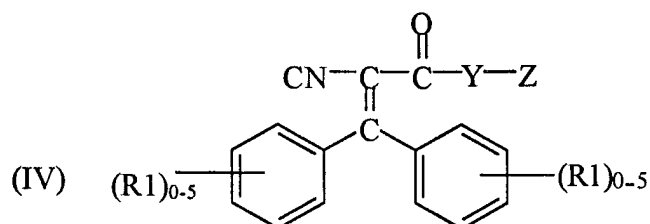
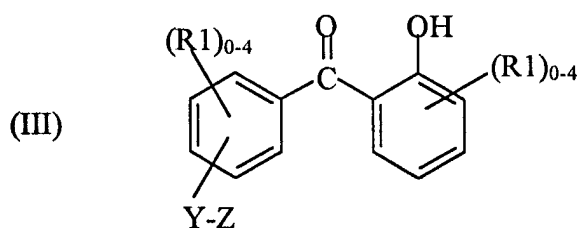


8. The ultraviolet light absorbing oligomer of claim 1 wherein at least one ultraviolet light absorbing compound is a compound of formula (IV).

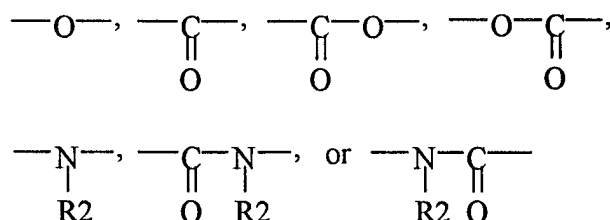
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9. A polymeric material comprising a polyolefin and an ultraviolet light absorbing oligomer, said ultraviolet light absorbing oligomer comprising the reaction product of a carboxyl functional oligomer and a hydroxy or amine functional ultraviolet light absorbing compound, wherein the ultraviolet light absorbing compound is a group of formula (I), (II), (III), or (IV):





- wherein each R1 is independently halogen, hydroxy, straight-chain or branched C₁₋₁₂ alkyl, straight-chain or branched C₂₋₁₂ alkenyl, straight-chain or branched C₁₋₁₂ alkoxy, straight-chain or branched C₂₋₁₂ alkenyloxy, straight-chain or branched C₁₋₁₂ alkanol, amino, straight-chain or branched C₁₋₁₂ alkylamino, or straight-chain or branched C₁₋₁₂ dialkylamino; Y is a C₁₋₁₈ alkylene or C₂₋₁₈ alkenylene group which may be straight-chain or branched and which may be interrupted by one or more



wherein each R2 is independently H or C₁₋₆ alkyl that may be straight-chain or branched; and Z is -OH or -NH₂.

10. The polymeric material of claim 9 wherein the polyolefin comprises an ethylene-acrylic acid copolymer.

11. The polymeric material of claim 9 wherein at least one ultraviolet light absorbing compound is a group of formula (I).

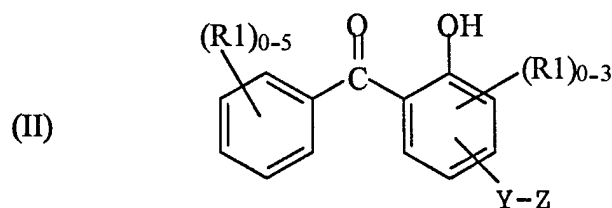
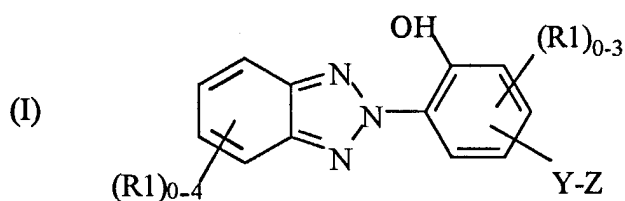
12. The polymeric material of claim 9 wherein at least one ultraviolet light absorbing compound is a group of formula (II).

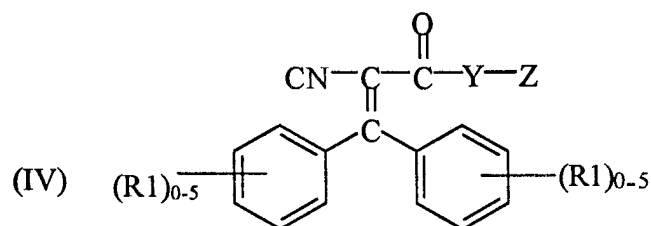
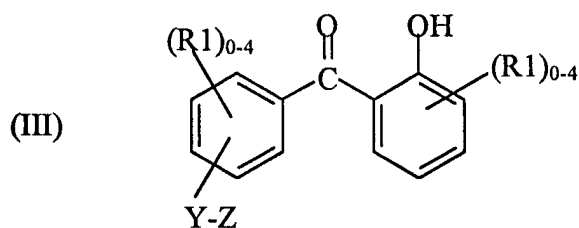
13. The polymeric material of claim 9 wherein at least one ultraviolet light absorbing compound is a group of formula (III).

14. The polymeric material of claim 9 wherein at least one ultraviolet light absorbing compound is a group of formula (IV).

15. A polymeric film comprising the polymeric material of claim 9.

16. A method of protecting a substrate from the effects of ultraviolet light, the method comprising applying a polymeric film to the substrate, said film comprising a polyolefin and the reaction product of a carboxyl functional oligomer and a hydroxy or amine functional ultraviolet light absorbing compound, wherein the ultraviolet light absorbing compound is a group of formula (I), (II), (III), or (IV):

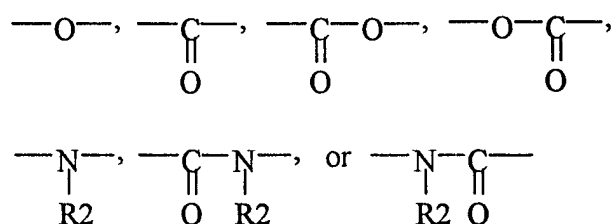




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wherein each R1 is independently halogen, hydroxy, straight-chain or branched C₁₋₁₂ alkyl, straight-chain or branched C₂₋₁₂ alkenyl, straight-chain or branched C₁₋₁₂ alkoxy, straight-chain or branched C₂₋₁₂ alkenyloxy, straight-chain or branched C₁₋₁₂ alkanol, amino, straight-chain or branched C₁₋₁₂ alkylamino, or straight-chain or branched C₁₋₁₂ dialkylamino; Y is a C₁₋₁₈ alkylene of C₂₋₁₈ alkenylene group which may be straight-chain or branched and which may be interrupted by one or more

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wherein each R2 is independently H or C₁₋₆ alkyl that may be straight-chain or branched; and Z is -OH or -NH₂.

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17. The method of claim 16 wherein the polyolefin comprises an ethylene-acrylic acid copolymer.

18. The method of claim 16 wherein the carboxyl functional polymer comprises an ethylene-acrylic acid copolymer.

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19. The method of claim 16 wherein the carboxyl functional polymer comprises acrylic acid, methacrylic acid, or a copolymer thereof.
- 5 20. The method of claim 16 wherein the ultraviolet light absorbing compound contains a benzotriazole group.
21. The method of claim 16 wherein the ultraviolet light absorbing compound contains a benzophenone group.
- 10 22. A conformable marking sheet comprising:
- (a) a top polymeric film layer having glass microspheres and skid resistant particles partially embedded therein, the film comprising a polyolefin and the ultraviolet light absorbing oligomer of claim 1;
- 15 (b) a base layer comprising a deformable thermoplastic polymer and a nonreinforcing mineral particulate;
- (c) a pressure sensitive adhesive layer; and
- (d) a release liner.
- 20 23. An enclosed-lens retroreflective sheeting comprising a layer of lenses anchored in a binder layer, a specularly reflective layer underlying the lenses, and a top layer comprising a polymeric film, said film comprising a polyolefin and the ultraviolet light absorbing oligomer of claim 1.
- 25 24. A reflective sign comprising the retroreflective sheeting of claim 23.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JS 97/14926

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F8/30 C08F8/14 C08L101/00 //(C08L101/00,23:26)

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 C08F C08L

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 4 981 914 A (MACLEAY RONALD E ET AL) 1 January 1991 see column 18, line 25 - line 40; claims ---	1-8
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 222 (C-302), 9 September 1985 & JP 60 084378 A (SHOWA DENKO KK), 13 May 1985, see abstract ---	1-8
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 113 (C-1033), 9 March 1993 & JP 04 298505 A (IPPOSHA OIL IND CO LTD), 22 October 1992, see abstract -----	1,9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

13 January 1998

Date of mailing of the international search report

20/01/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/14926

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