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(54) RADIATION TREATED PROPYLENE POLYMERS

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HIGH ENERGY RADIATION TREATED STABILIZED PROPYLENE POLYMERSABSTRACT

5 A propylene polymer molding composition which is resis-
tant to high energy radiation induced discoloration and losses of
physical properties is obtained by incorporation of a phenolic
isocyanurate compound as a stabilizer, in conjunction with a thio-
synergist, and preferably a stearate.

BACKGROUND OF THE INVENTION

This invention relates to compositions of propylene polymers suitable for high energy radiation treatment. One aspect of the invention relates to propylene polymer compositions of specific characteristics which have been subjected to sterilizing dosages of high energy radiation, such as gamma radiation.

Propylene polymers, and specifically those of a substantial crystalline content have been applied to many new uses, which uses have required that the polymer be processed or treated in a particular manner. For example, propylene polymers generally have the contact clarity, heat distortion resistance and low chemical reactivity required by manufacturers of medical single-use items such as syringes, forceps, surgical clamps and various instrument trays, etc., used in the operating room. Obviously, before any such articles can be safely used, it is required that it be sterilized.

Ethylene oxide has the sterilizing effectiveness needed by these same manufacturers, and until recently was regarded as

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generally safe. Recently, however, ethylene oxide has come under increasing scrutiny by the authorities, since it is believed to be a mutagen and possibly a carcinogen. Acceptable limits of residual ethylene oxide and its by-products have therefore been lowered. In addition, the cost of ethylene oxide is rising, and the sterilizing costs (because of a 14-day holding requirement and the individual batch testing requirement) are becoming non-competitive.

High energy radiation, on the other hand, leaves no residue and has a dose-related sterilization rate which permits immediate release upon certification of the dose. However, unlike ethylene oxide, radiation, especially γ -radiation, damages the polymer, in that it causes either embrittlement or discoloration or both of these effects occur simultaneously. As disclosed in U.S. Patent No. 3,537,967 and in its Canadian counterpart Canadian Patent No. 811,766, the discoloration is attributable to the use of phenolic antioxidants in the compositions to prevent or minimize the radiation induced degradation of the polymer. Even worse discoloration is obtained with additive systems containing a phenolic antioxidant and a thiodipropionic ester synergist. The patents teach that discoloration resistance upon high energy radiation is achieved by the incorporation into the polymer of the ester of thiodipropionic ester as the sole stabilizer. However, these compositions have been found not to be entirely satisfactory especially for use in the fabrication of syringes, in that the strength retention (flexural strength) of the irradiated polymer is minimal even at high levels of thiodipropionic ester incorporation, and the sterilized article becomes so embrittled, that it is prone to breakage in use. Also, because of the known lesser efficiency of thiosynergists in providing long term stability against oxidative degradation of propylene polymers as compared to that of phenolic antioxidants, the shelf life of articles manufactured from the compositions of U.S. Patent No. 3,537,967 and Canadian Patent No. 811,766 is not as long as would be desired.

Hirao in U.S. Patent No. 3,940,325 teaches that the disadvantages of the compositions of the aforementioned patents can

be overcome provided that as phenolic antioxidant an additive selected only from either octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate or/and tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane be used. Many other propylene polymers containing combinations of various antioxidant thiosynergist and lubricant additives were tested by Hirao at various concentration levels and were found to be deficient, including those containing phenolic isocyanurate stabilizers.

According to Gilles in U.S. Patent No. 3,644,277, such isocyanurate compounds provide stability against oxidative, thermal and photochemical degradation, but nothing is said regarding the effectiveness of the additives during high energy radiation. Gilles also teaches that synergistic activity is obtained when his specific isocyanurates are combined with thiosynergists such as the well known diesters of β -thiodipropionic acid of the aforementioned U.S. Patent No. 3,537,967. In order to achieve this beneficial synergistic effect the weight ratio of thiosynergist to isocyanurate stabilizers should be between about 1:1 and up to about 5:1. This ratio range is typical for most other antioxidant thiosynergist combinations, e.g. those shown and discussed by Hirao in U.S. Patent No. 3,940,325.

It is an object of the present invention to provide novel compositions of matter of polymers of propylene which are resistant to discoloration and to degradation of physical properties upon high energy radiation treatment.

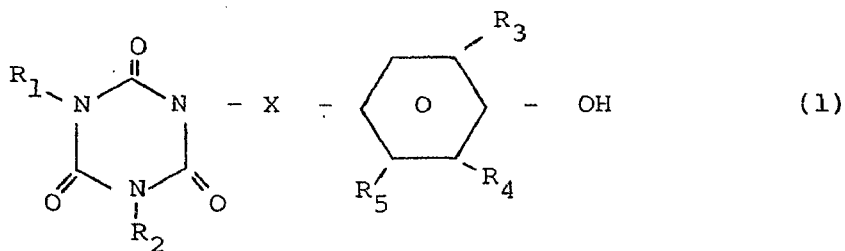
It is a further object of this invention to provide shaped articles of polymers of propylene which can be used for medical or food packaging purposes, which shaped articles have been subjected to a sterilizing dose of high energy radiation.

THE INVENTION

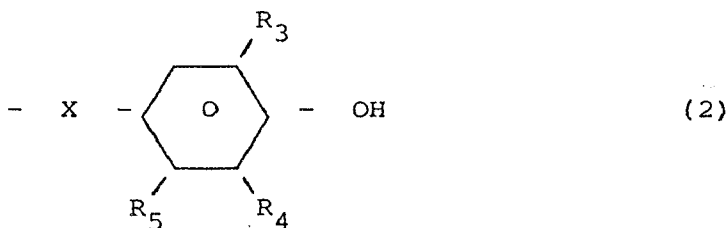
The above objects are unexpectedly accomplished by incorporating into a propylene polymer (a) from about 200 to about 400 ppm of a phenolic antioxidant containing an isocyanurate group

in its molecular structure, (b) a thiosynergist in an amount which is at least 6 times the amount of the antioxidant of (a), and subjecting the resulting composition to a dose of high energy radiation.

5 Illustrative examples of phenolic antioxidants containing an isocyanurate group in the molecular structure are those having the general formula:



wherein R_1 and R_2 independently from each other are either hydrogen, an alkyl group of from 1 to 5 carbon atoms, or a group represented by the formula:



20 wherein R_3 , R_4 , and R_5 independently from each other are either hydrogen or a lower alkyl group containing from 1 to 5 carbon atoms, and X is a hydrocarbon linking group.

Preferably, R_1 and R_2 are both groups represented by the formula (2) given above. R_3 and R_4 are preferably alkyl groups and most preferably tertiary alkyl groups such as t-butyl and t-amyl.

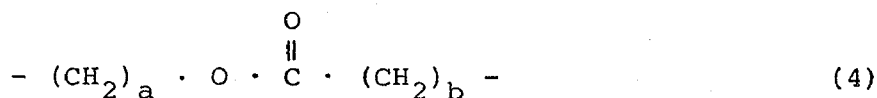
25 The linking group -X- can generally be any hydrocarbon group providing the necessary linkage between the isocyanurate group and the phenolic group.

For instance, X can be a group represented by the formula:



wherein R_6 and R_7 independently from each other can be either hydrogen or an alkyl group having from 1 to 6 carbon atoms. Phenolic antioxidant compounds containing such linking groups are known in the art and can be prepared e.g. by the condensation reaction of a phenol (containing the $R_3 - R_5$ groups as defined above), an appropriate aldehyde and isocyanuric acid (containing the R_1 and R_2 groups defined above) with the formation of water as byproduct.

Other suitable X groups include those represented by the formula:

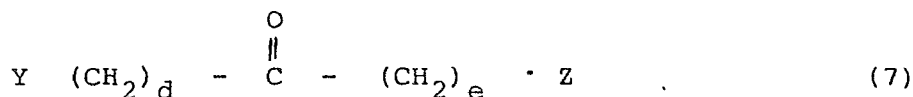
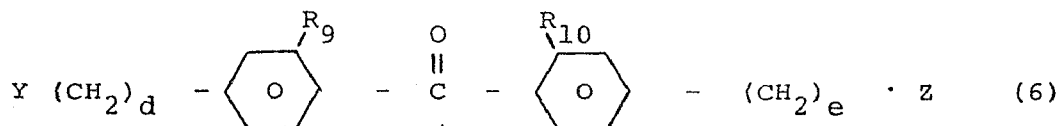
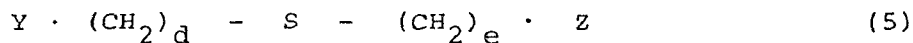


wherein a and b independently from each other are each at least 2 and a + b ranges from 4 to 18.

Compounds containing these linking groups are also well known in the art. Generally, the compounds can be prepared by first reacting a phenol, (as defined before), with an appropriate ester having the formula $CH_2 = CH \cdot (CH_2)_{a-2} \cdot COOR_8$ wherein R_8 is a lower alkyl group such as methyl, ethyl, propyl or butyl (the base catalyzed Michael reaction).

In a separate step an isocyanuric acid (as defined before) is reacted with a halogen-substituted alkanol or thiol of the general formula $Y \cdot (CH_2)_b \cdot Z$ wherein Y is a halogen and Z is either -OH or -SH. After removal of byproduct HY, e.g. HCl when the halogen is chlorine, the reaction products from the above described two steps are reacted with each other forming the desired compound and the corresponding R_8 alcohol or thiol as byproduct.

Analogous procedures can obviously be used in preparing many other phenolic antioxidant compounds having additional groups present in the linking group, for instance, by the use of other halogen substituted alkanols or thiols such as



wherein d and e each are an integer of at least 2

d + e ranges from 4 to 6,

and a + d + e ranges from 6 to 18,

R₉ and R₁₀ each are either hydrogen or a hydroxyl group.

The phenolic compounds preferably employed in this invention are those having the linking groups - X - defined by formulae (3) and (4) above, e.g. tris (3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate and 3,5-di-t-butyl-4-hydrocinnamic acid triester with 1,3,5-tris (2-hydroxyethyl)-S-triazine-2,4,6 (1H, 3H, 5H)-trione. These compounds are commercially available.

In addition to the above specified phenolic antioxidants the propylene polymer composition also contains a thiosynergist in amounts at least 6 times the weight of the antioxidant and generally in concentrations ranging from about 1200 ppm to about 3500 ppm. The thiosynergist is a dialkyl ester of thiodipropionic acid wherein the alkyl radicals contain from 4 to 22 carbon atoms. Particularly suitable diesters are those having alkyl groups containing 18 carbon atoms namely distearyl thiodipropionate and 22 carbon atoms namely dilauryl thiodipropionate.

A metal stearate such as calcium stearate or zinc stearate, is advantageously also incorporated as a processing aid, usually in amounts ranging from about 300 to about 700 ppm.

5 The polymers of propylene applicable for use in this invention are homopolymers of propylene and random or block copolymers of propylene with other mono- α -olefins such as ethylene, butene-1 and higher homologues containing up to 10 carbon atoms. Blends of such propylene polymers with other polymers such as polyethylene are also included within the scope of this invention. 10 Generally the proportion of polymerized propylene in the total resin phase of the composition should be at least 60% by weight.

The propylene polymer compositions can be pigmented, if so desired. No significant distortion of color is observed after exposure to sterilizing doses of high energy radiation, e.g. 15 phthalocyanine blue pigmented articles of manufacture retain their brilliant colors without development of green tones.

In general, the radiation treatment can be applied to polymers of propylene useful particularly for medical purposes; however, this should not be understood to be a limiting factor as 20 the radiation treatment can be applied to the propylene polymers for any use for which such a treatment is required, such as for meat packaging, preserving food in retort packages and other uses.

The high energy radiation is conveniently provided by a cobalt 60 source. Other radiation treatment, however, can be used, 25 such as high energy X-rays, or high energy electrons (β -radiation). In general, radiation dosages that can be applied range up to about 5 megarads. For sterilization purposes, it has been found that an article of manufacture such as a syringe can be effectively sterilized by applying 2 megarads under gamma radiation. 30

The following examples illustrate the invention without limiting it.

EXAMPLES 1 - 3

A propylene homopolymer resin having a melt flow of 4-5 g/10 min. was melt blended with 300 ppm by weight of a commercially available phenolic isocyanurate Good-rite® 3125 (which is the 3,5-di-t-butyl-4-hydroxy-hydrocinnamic triester of 1,3,5-tris(2-hydroxy ethyl)-S-triazine-2,4,6 (1H, 3H, 5H -trione), 2000 ppm of either dilaurylthiodipropionate (DLTDP) or distearylthiodipropionate (DSTDP) and 500 ppm of either calcium stearate or zinc stearate. Tensile bar specimens (2 1/2" x 1/2" x 60 mil) were prepared from each of these blends and were then subjected to gamma irradiation with doses of 0, 1, 3 and 5 megarads respectively employing a cobalt 60 source. Subsequently the specimens were tested for brittleness using a 2 x 180° manual flex test, in which the grip tab of the test bar is first bent 180° to one side and then bent back to the other side at 180°. The test is passed if neither a complete break nor a fibrous hinge results from the two bendings. The yellowness index (ASTM D- 1925) the tensile properties (ASTM D- 1708) were also determined. The pertinent data are shown in Table 1 below.

TABLE 1

Ex. No.		1	2	3
	Additives - ppm			
5	Good-rite [®] 3125	300	300	300
	DLTDP	-	2000	2000
	DSTDP	2000	-	-
	Ca Stearate	500	-	500
	Zn Stearate	-	500	500
	Properties			
10	2 x 180° flex			
	0 Mrad	←————— Passed —————→		
	1 Mrad	←————— Passed —————→		
	3 Mrad	←————— Passed —————→		
	5 Mrad	←————— Passed —————→		
15	Yellowness Index			
	0 Mrad	-0.3	-0.4	-0.4
	1 Mrad	-	-	-
	3 Mrad	-	1.8	2.0
	5 Mrad	3.2	5.0	5.1
20	Tensile Yield - psi			
	0 Mrad	5381	5685	5228
	1 Mrad	5282	5436	5456
	3 Mrad	5448	5137	5430
	5 Mrad	5290	5541	5230
25	Tensile Fail - psi			
	0	4796	4338	4401
	1	4096	4338	4483
	3	3851	4176	3961
	5	3680	3659	3680
30	% Elongation			
	0 Mrad	248	240	267
	1 Mrad	218	208	236
	3 Mrad	215	106	198
	5 Mrad	189	41	175

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The above compositions compared favorably with polypropylene compositions stabilized solely with either DLTDP or DSTDP at 1400 to 3500 ppm incorporation in that the very pale and acceptable color developments (3-5YI) after irradiation at sterilizing doses of 5 megarads were about the same or at most slightly higher, while the physical properties were considerably improved over the comparison compositions, which were brittle and failed the manual flex test.

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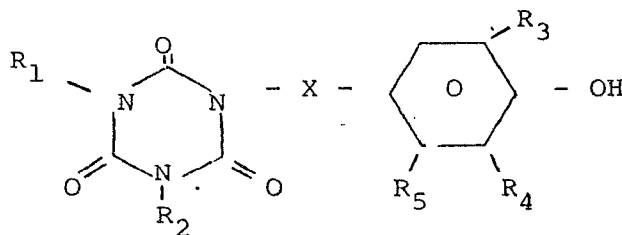
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Resort can be made to modifications and equivalents
falling within the scope of the appended claims.

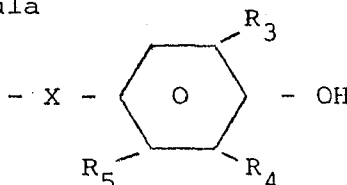
WHAT IS CLAIMED IS:

1. A method for imparting improved strength and discoloration resistance to a stabilized, high energy radiation treated propylene polymer which comprises incorporating into said propylene polymer as a stabilizer from about 200 to about 400 ppm of a phenolic antioxidant containing an isocyanurate group in its molecular structure and a thiosynergist in an amount of at least 6 times the weight of said stabilizer prior to subjecting said propylene polymer to a sterilizing dose of high energy radiation.

2. The method of claim 1, in which the phenolic antioxidant has the formula



wherein R_1 and R_2 independently from each other are either hydrogen, an alkyl group of 1 to 5 hydrocarbons or a group represented by the formula



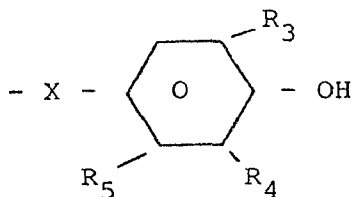
R_3 , R_4 and R_5 independently from each other are either hydrogen or an alkyl group of from 1 to 5 carbon atoms, and X is a hydrocarbon linking group.

3. The method of claim 1, wherein the thiosynergist is a dialkyl ester of thiodipropionic acid and is present in amounts from about 1200 to about 3500 ppm.

4. The method of claim 1, wherein from about 300 to about 700 ppm of calcium stearate or zinc stearate is incorporated into the propylene polymer prior to subjecting said propylene polymer to the high energy radiation.

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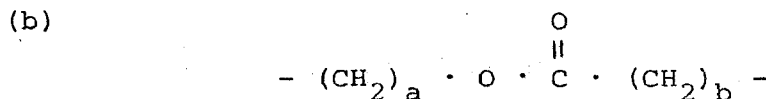
5. The method of claim 2, wherein R_1 and R_2 are both a group represented by the formula



6. The method of claim 2, wherein R_3 and R_4 are alkyl groups.
7. The method of claim 2, wherein R_3 and R_4 are tertiary alkyl groups.
8. The method of claim 2, wherein $-\text{X}-$ is selected from the groups represented by the formulae



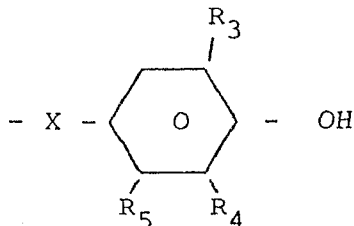
wherein R_6 and R_7 independently from each other is either hydrogen or an alkyl group having from 1 to 6 hydrocarbons, or



wherein a and b independently from each other are at least 2 and $a + b$ ranges from 4 to 18.

9. The method of claim 2 wherein the phenolic antioxidant is selected from tris (3,5-di-*t*-butyl-4-hydroxybenzyl) isocyanurate or 3,5-di-*t*-butyl-4-hydrocinnamic triester with 1,3,5-tris(2-hydroxy ethyl)-*S*-triazine-2,4,6 (1H, 3H, 5H)-trione.
10. The method of claim 1, wherein said high energy radiation is gamma radiation.
11. The method of claim 10, wherein the sterilizing dose is at least about 2 megarads and up to 5 megarads.

17. The article of claim 14, wherein R_1 and R_2 are both a group represented by the formula

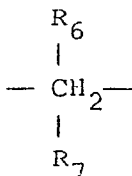


18. The article of claim 14, wherein R_3 and R_4 are alkyl groups.

19. The article of claim 14, wherein R_3 and R_4 are tertiary alkyl groups.

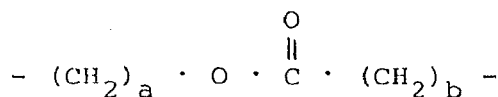
20. The article of claim 14, wherein $-\text{X}-$ is selected from the groups represented by the formulae

(a)



wherein R_6 and R_7 independently from each other is either hydrogen or an alkyl group having from 1 to 6 hydrocarbons, or

(b)



wherein a and b independently from each other are at least 2 and $a + b$ ranges from 4 to 18.

21. The article of claim 14 wherein the phenolic antioxidant is selected from tris (3,5-di-*t*-butyl-4-hydroxybenzyl) isocyanurate or 3,5-di-*t*-butyl-4-hydrocinnamic triester with 1,3,5-tris (2-hydroxy ethyl)-*S*-triazine-2,4,6 (1H, 3H, 5H)-trione.
22. The article of claim 13, wherein said high energy radiation is gamma radiation.
23. The article of claim 22, wherein the sterilizing dose is at least about 2 megarads and up to 5 megarads.

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24. The article of claim 16, wherein the thiosynergist is either distearylthiodipropionate or dilaurylthiodipropionate.



SUBSTITUTE

REPLACEMENT

SECTION is not Present

Cette Section est Absente