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<p>(54) Title: DEGRADABLE THERMOPLASTIC COMPOSITIONS AND BLENDS</p> <p>(57) Abstract</p> <p>The invention provides a compostable thermoplastic polymer composition comprising a thermoplastic polymer, a transition metal salt selected from cobalt, manganese, copper, cerium, vanadium and iron, and a fatty acid or ester having 10 to 22 carbon atoms providing unsaturated species and free acid. The composition will oxidatively degrade to an embrittled state within at least 14 days at 60 °C and a relative humidity of at least eighty percent.</p>		

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DEGRADABLE THERMOPLASTIC COMPOSITIONS AND BLENDS.

Background and Field of the Invention

10 This invention relates to a novel polymeric blend having enhanced environmental degradability properties comprising a non-biodegradable thermoplastic polymer.

There are numerous patents dealing with
15 enhancing the degradability of conventional non-biodegradable polymers such as polyolefins by use of additive systems. These additive systems are quite frequently designed to enhance the polymers degradability in a specific type of environment and
20 over a specific length of time. For example, U.S. Patent No. 3,840,512 (Brackman) exemplifies prodegradant systems comprising ferric stearate with various free fatty acids, both saturated and unsaturated. Manganese stearate is also exemplified in
25 a system with stearic acid. Brackman states that thermoplastic films (e.g., polyolefin films) formed with these prodegradant systems will embrittle when exposed to artificially UV-activated irradiation at times ranging from 2 to 35 days. It is specifically
30 stated that the nature of the hydrocarbon group on the fatty acid does not have a large influence on the rate of UV degradation. Brackman does not address the issue of degradability in other environments, such as in a compost environment. A patent dealing with a similar
35 prodegradant system, U.S. Patent No. 4,067,836 (Potts et al.), discloses adding a transition metal salt, an auto-oxidative susceptible additive, and an anti-oxidant to polyethylene. The only exemplified auto-oxidative susceptible additives were polypropylene and
40 polyethylene oxide (which did not work as acceptably as polypropylene). The degradation of the samples was

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tested by exposure to an artificial solar light spectral distribution. The degradability characteristics of these prodegradant additives were never demonstrated in other environments such as a
5 compost environment. Generally, additive systems as described above, designed to make a polymer degrade when exposed to environmental radiation, have proved of doubtful practical utility. Only a relatively small portion of the waste stream is ever exposed to
10 sunlight, even for short periods of time.

In U.S. Patent No. 3,921,333 (Clendinning, et al.) it is proposed to make the composition of Potts, et al., discussed above, degradable in a soil type environment by adding a biodegradable polymer such as
15 poly(caprolactone). The invention described is allegedly useful for materials such as transplanting containers, mulch film and the like. Again, only a small portion of the plastic in the waste stream is ever used in such environments and as such the
20 compositions described are of limited applicability based on their limited intended use.

U.S. Patent No. 4,038,228 (Taylor, et al.) describes placing a transition metal salt of an unsaturated organic acid or ester into a polymer film
25 (e.g., polyethylene or polypropylene) to enhance its degradability in the absence of sunlight. The transition metal salts discussed are identical to many of those exemplified in the above Clendinning et al. and Potts et al. patents; however, they are exemplified
30 at extremely high concentrations. The exemplified film degrades to an embrittled condition within three days at room temperature. Such a film is of doubtful utility as it would likely degrade before use and the exemplified high concentrations of cobalt used would
35 create an extremely costly and toxic material.

A more recent patent, U.S. Patent No. 4,931,488 (Chiquet), describes a polymer (e.g.,

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polyethylene) composition which allegedly will degrade when exposed to heat, ultraviolet radiation, sunlight, or under composting conditions. The prodegradant system broadly described consists of a biodegradable substance such as starch, an iron compound and a fatty acid or fatty acid ester, optionally with copper stearate. The exemplified films, however, are limited to polyethylene blended with ferric stearate and soya oil, with a minor proportion of cupric stearate in certain examples. Although it is alleged that these compositions are tested under composting conditions, the conditions are not actually set forth and the reported films do not appear to degrade for up to twenty weeks, a situation which would be unacceptable in most commercial composting situations where peak temperatures are reached for only approximately two weeks.

As can be seen the art continues to seek to improve the degradability of conventional plastic films in various environments by use of additive prodegradant systems. These systems have been designed to provide degradability properties in a wide variety of environmental conditions. Systems that have been found to work in one set of conditions do not necessarily work under a separate set of conditions which can vary from a dry sunlit exposure to the wet, dark, and relatively infertile conditions of a composter. Applicants have found a composition which will rapidly degrade under conditions of a typical commercial composting unit yet provide an article, such as a film, which is functional under normal use conditions. A typical composting unit generally is exposed to peak temperatures of greater than 60°C for periods of approximately two weeks or less. During that period, the organic matter in the composter is generally exposed to an extremely high humidity, generally close to one hundred percent. These humidity conditions are

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generally favorable for biological attack, however, these conditions are generally inhospitable to oxidative type degradations where transition metal salts are typically employed.

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BRIEF SUMMARY OF THE INVENTION

The present invention provides a degradable composition comprising a thermoplastic polymer, a transition metal salt selected from salts of cobalt, manganese, copper, cerium, vanadium and iron, and a fatty acid or ester having ten to twenty-two carbon atoms, comprised predominantly of unsaturated species and comprised at least partially of free acid. The composition is designed so that it will oxidatively degrade to form an embrittled or very low tensile strength polymer within at least fourteen days at 60°C and at a relative humidity of at least eighty percent. After this peak period, the temperature of a typical compost unit slowly declines, decreasing the rate of oxidative degradation, often quite dramatically.

DETAILED DESCRIPTION

Generally, the invention is directed to a compostable thermoplastic polymer composition comprising a thermoplastic polymer containing a prodegradant system of an auto-oxidant of an unsaturated fatty acid or ester having ten to twenty-two carbon atoms, and certain transition metal salts.

The fatty acid or ester is present in the polymer composition at a concentration of about 0.1 to 10 weight percent so as to provide a concentration of unsaturated species of greater than 0.1 weight percent and a concentration of free acid species greater than 0.1 percent by weight based on the total composition. Further included is a transition metal salt at a relatively low concentration of 5 to 500 ppm of the metal itself where the transition metal is selected

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from the group comprising cobalt, manganese, copper, cerium, vanadium and iron, preferably cobalt, manganese, copper or cerium. The composition is formulated such that it will oxidatively degrade, preferably to an embrittled state, within fourteen days at a temperature of about 60°C and relative humidity of 80 percent or more, preferably 100 percent after a reasonable shelf life. Generally, it is expected that the composition will have to be shelf-stable for a time ranging from one week to 12 months. As the degradation occurs slowly, even at room temperature, for longer shelf-life products, generally lower concentrations of the transition metal or fatty acid (free acid and/or unsaturated species) will be required to provide a compostable film at the film's intended mean shelf life. Conversely, higher concentrations of the metal or fatty acid species will be required for films with short intended shelf lives.

Thermoplastic polymers suitable for use with the present prodegradant system include polyolefins such as polyethylene, polypropylene, polybutylene or poly(4-methyl-1-pentene). Other suitable polymers include poly(vinyl acetates), polyesters (e.g., aliphatic polyester), polyurethanes (e.g., aliphatic polyurethanes), poly(vinyl alcohols), polyamides (e.g., aliphatic polyamides), polystyrenes or polyamines. Copolymers and blends are also suitable. Preferably, the polymer employed is a saturated thermoplastic polymer, such as polyethylene or polypropylene, suitable for extrusion or coextrusion. Most preferred are polypropylenes or polypropylene blends, such as blends of polypropylene and polyethylene-based polymers and copolymers.

The transition metal salts include those discussed, for example, in U.S. Patent No. 4,067,836, which salts can be ones having organic or inorganic ligands. Suitable inorganic ligands include chlorides,

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nitrates, sulfates, and the like. Preferred are organic ligands such as octanoates, acetates, stearates, oleates, naphthenates, linoleates, tallates and the like. Although a wide range of transition metals have been disclosed in the art as suitable for various prodegradant systems, for a compostable polymeric film it has been found that the transition metal must be selected from the group comprising cobalt, manganese, copper, cerium, vanadium and iron in a concentration range of from 5 to 500 ppm and preferably cobalt, manganese, copper and cerium for most polymers. Preferably, the transition metal is used in a concentration of from 5 to 200 ppm which is highly desirable as such metals are generally undesirable in large concentrations. High transition metal concentrations in compost material can lead to toxicological and environmental concerns due to groundwater leaching of these heavy metals into the surrounding environment. Further, higher transition metal concentrations can yield unstable films with the invention prodegradant system.

Oxidative degradation in a typical composter occurs under substantially saturated atmospheric humidity conditions. The plastic on its external face will normally see a humidity of approximately 100 percent. These are extremely severe conditions for oxidative degradation and it has been found that the prodegradant systems described in the art are not suitable for adequate degradation of plastics under these conditions.

It is found that adequate degradation under typical commercial composting conditions requires salts of the above mentioned transition metals in combination with acid moieties such as those found in unsaturated fatty acids. It has also been found that unsaturation in the fatty acid, or an admixed fatty acid ester or natural oil, is required to produce adequate

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degradation with the proper transition metal compound. Preferably, this unsaturated fatty acid is present in the polymer composition at concentrations of at least 0.1 weight percent of the composition, preferably at
5 least 0.25 weight percent, and most preferably at least 0.5 weight percent. Also suitable are blends of fatty acids and fatty acid esters or oils as long as the amount of free acid and unsaturated species are generally equivalent to the above described ranges for
10 a pure fatty acid containing composition.

Generally, it has been found that unsaturated fatty acids having 10 to 22 carbon atoms function well in providing the degradation rate required for a compostable material. Unsaturation such as found in
15 abnormal oils is found to be preferred. Such unsaturation includes two or more double bonds in the fatty acid or ester chains. Generally, unsaturation where two of the double bonds are separated by two single bonds, resulting in a doubly allylic carbon
20 atom, has been found to be highly desirable, although conjugated double bonds are also preferred. Samples of materials which contain doubly allylic carbon atoms include linseed oil, linoleic acid and linolenic acid. An example of a common conjugated fatty acid is
25 eleostearic acid found in high concentration, in the ester form, in natural tung oil. Other natural oils containing fairly high amounts of unsaturation include fish oils such as sardine, cod liver, manhaden, and herring oil. Fatty acids derived from these naturally
30 occurring oils containing high percentages of unsaturation are also suitable as auto-oxidative accelerating components.

Also suitable are fatty acid derivatives, substituted fatty acids or derivatives or corresponding
35 reduction products such as amines or alcohols and the like, although substitutions should not be adjacent to allylic or conjugated double bonds or other sources of

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unsaturation as this tends to reduce the effectiveness of such fatty acids and derivatives. Generally, other acids have been found to be unsuitable, including dicarboxylic fatty acids. However, additive amounts of
5 rosin acids such as Foral™ AX have been found to be useful in some instances.

Preferably, the composition further includes an anti-oxidant. Anti-oxidants help stabilize the polymer during extrusion operations during the
10 formation of a film or other article as well as help provide a suitable shelf life for the degradable articles. Any suitable anti-oxidants used with the conventional base polymer are acceptable including typical anti-oxidants such as sterically hindered
15 phenols, aryl amines, thioureas, thiocarbamates, thioetheresters, phosphites, or the like. Illustrative anti-oxidants can be found, for example, in U.S. Patent No. 4,067,836. Preferably the anti-oxidant is present in a concentration of approximately 0.1 weight percent
20 or more based on the total polymer composition and the intended shelf life.

The compostable polymer composition also preferably includes a naturally biodegradable polymer such as poly(caprolactone), poly(lactic acid),
25 poly(hydroxybutyrate-valerate), poly(ethylene adipate), poly(vinyl alcohol), modified starch/oleofin copolymers, poly(propylene oxide), and poly(ethylene oxide). Other suitable biodegradable polymers are generally well known and are described in, for example,
30 U.S. Patent No. 3,921,333. These biodegradable polymers assist in further biodegradation of the composition following the transition metal salt catalyzed oxidative degradation, which reduces the base thermoplastic resin to a lower molecular weight
35 substance. Although these biodegradable polymers alone can be broken down fairly rapidly in any compost type environment, their physical properties are generally

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inferior to those of conventional thermoplastic films. Further, their costs are often prohibitive for use in typical commercial applications. However, blended with conventional thermoplastic materials, such as

5 polyolefins, these biodegradable polymers should assist in the biological breakdown of the articles following the catalytic embrittlement period. Generally, the naturally biodegradable polymers can be included in amounts from 5 to 50 weight percent of the composition,

10 preferably these biodegradable polymers are used at from 5 to 25 weight percent.

Other conventional additives can be added to the polymer composition including fillers, dyes, pigments, anti-blocking agents or the like.

15 The invention composition finds particularly advantageous use for producing films or fibers due to the composition's ability to be extruded without significantly affecting performance. With such extruded films or fibers, the fatty acid species

20 preferably are predominantly C₁₂ to C₂₂ species. These fatty acid species are generally more tolerant of typical film or fiber extrusion conditions. However, the composition can be used in other extruded articles or non-extruded articles.

25 Typical uses for the composition as extruded films or fibers include disposable items used at ambient conditions or below, or exposed to elevated temperatures for a relatively short period of time. This would include trash bags, disposable diaper

30 components (e.g., diaper backsheets, polymer film components, extruded nonwoven fiber webs, and the like), freezer bags, disposable medical bags or components, disposable garments, hygiene articles, internal packaging films, etc.

35 The following examples are provided to illustrate presently contemplated preferred embodiments

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for practicing the invention, but are not intended to be limiting thereof.

TEST PROCEDURES

5 Embrittlement

Embrittlement was determined by hand testing the samples. A state of embrittlement was defined as the time at which the samples had little or no tear or tensile strength remaining or would crumble when
10 folded. With softer or lower melting polymers, such as polyethylene, the films did not generally disintegrate or crumble but rather became soft and lost all tensile strength.

Compost conditions were simulated by placing
15 the films into a jar of water which was then buffered to a pH of 6 by a phosphate buffer and heated to various temperatures. Samples were removed at various times and dried and tested for embrittlement. Generally, these samples were tested at intervals of
20 12-24 hours.

Film Preparation

All films were prepared on a 3/4" (1.9 cm) HAAKE™ extruder having a L/D ratio of 24:1 using 3
25 zones having temperatures of 390°F (199°C), 410°F (210°C), and 430°F (221°C) with a die temperature of 430°F. The film was formed on a casting roll at a temperature of 70°F (21°C). The films were taken off the roll so as to have a total thickness of 4.0 mils
30 (102μ).

Examples 1-14

The films were prepared as described above using 566 parts per million of manganese stearate
35 (i.e., 50 ppm manganese), and 1 weight percent of the indicated natural oils (Table 1) in polypropylene (a Shell 5A95 9.5 MFI homopolymer with an anti-oxidant

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available from Shell Chemical Co., Houston, TX) with the exception of Example 14 which utilized 2 percent of a styrene-butadiene rubber (SBR) as an auto-oxidant. The SBR was incorporated as a concentrate consisting of 5 28% SBR in 72% Shell 7C04N PP/PE impact copolymer (35 MFI, 9% polyethylene).

Two inch (5 cm) by six inch (15 cm) samples were placed in trays in dry forced air ovens. The trays were removed periodically, and the films were 10 creased by hand. Embrittlement was defined as the point in time when the samples would first crack and fall apart when creased. In the tables provided, the greater than sign indicates that the testing was terminated at the noted time (in hours). The samples 15 were tested at 60°C, 70°C and 88°C, as noted in Table 1 below.

TABLE 1

20	<u>Example</u>	<u>Auto-Oxidant</u>	<u>Time to Embrittlement (Hours)</u>		
			<u>88°C</u>	<u>70°C</u>	<u>60°C</u>
	1	Coconut Oil	55	257	600
	2	Almond Oil	12	202	317
25	3	Olive Oil	36	202	410
	4	Castor Oil	55	179	317
	5	Safflower Oil	31	161	245
	6	Soy Oil	5	161	291
	7	Wheat Germ Oil	4.5	161	358
30	8	Walnut Oil	6	130	291
	9	Dehydrated Castor Oil	4.5	130	317
	10	Cod Liver Oil	12	94	190
	11	Sardine Oil	11	57	149
	12	Tung Oil	7	53	150
35	13	Linseed Oil	6	20	59
	14	SBR	26	77	145

40 All samples were approximately 1-2 weeks old when tested. The table indicates that the oils containing more highly unsaturated fatty acid esters

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provide the fastest high temperature degradation at typical dry conditions.

Examples 15-28

5 Various films were prepared and tested, as described above for Examples 1-14, using 1 weight percent of various fatty acids and fatty acid derivatives as the auto-oxidants. All auto-oxidants were C₁₈ fatty acids or fatty acid derivatives with 0, 1
10 and 2 double bonds (stearic, oleic and linoleic, respectively). The samples were approximately 1-2 weeks old when tested. The results are given in Table 2. The results indicate that substitution on the fatty acid generally does not significantly effect the
15 degradation rate of compositions using substituted derivatives of typical fatty acids.

TABLE 2

20	<u>Example</u>	<u>Auto-Oxidant</u>	<u>88°C</u>	<u>70°C</u>	<u>60°C</u>
	15	Stearic Acid (C18,0 DB)	8-23	217	155
	16	Methyl Stearate	>800	>800	>800
	17	Ethyl Stearate	>800	>800	>800
25	18	Propyl Stearate	8-23	103	155
	19	Stearamide	8-23	265	348
	20	Stearylamine	8-23	>800	>800
	21	Stearyl Alcohol	8-23	103	204
	22	Oleic Acid (C18,1 DB)	3.5	9-23	48
30	23	Propyl Oleate	8-23	48	120
	24	Oleamide	30	48	102
	25	Oleyl Alcohol	8-23	38	102
	26	Linoleic Acid (C18,2 DB)	5.5	23	38
	27	Methyl Linoleate	10	38	78
35	28	Propyl Linoleate	10	38	116

The examples were also checked for degradation after storing at room temperature for 8.5
40 months. Examples 22 and 24-28 showed signs of embrittlement, however, Examples 15-21 and 23 were not embrittled at this date.

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Examples 29-62

Samples were prepared, as described above for Examples 1-14, using various polypropylenes (unstabilized and stabilized, i.e., commercially available resins with anti-oxidants), stabilized polyethylenes and blends thereof, as indicated in Table 3, using the procedure outlined above. All metals were added as metal stearates to provide the indicated concentration of metal. Samples were then placed in water jars and buffered to a pH of 6 using a phosphate buffer. The samples were tested for embrittlement as described above for Examples 1-14, except for the polyethylenes and blends, which were tested for softness and loss of tensile strength. The time for embrittlement is shown in Table 3 below. The samples were tested within one week after extrusion.

TABLE 3

Ex. No.	Composition	88°C		60°C		49°C	
		Hrs.	Hrs.	Hrs.	Hrs.	Hrs.	Hrs.
29	5A95 PP + 50ppm Co + 4% Oleic acid,	<16		43		85	
30	Unst. PP + 50ppm Mn + 4% Oleic acid	16		40		85	
31	Unst. PP + 50ppm Fe + 4% Oleic acid	16		65		88	
32	5A95 PP + 50ppm Co + 2% Linseed oil + 2% Stearic acid	20		88		140	
33	Unst. PP + 50ppm Fe + 2% Linseed oil + 2% Stearic acid	40		85		85	
34	5A95 PP + 50ppm Mn + 4% Oleic acid	40		110		195	
35	Unst. PP + 50ppm Fe + 4% Stearic acid	40		134		165	
36	5A95 PP + 50ppm Mn + 4% Linoleic acid	42		46		88	
37	5A95 PP + 50ppm Mn + 2% Linseed oil + 2% Oleic acid	42		96		120	
38	5A95 PP + 50ppm Mn + 2% Linseed oil + 2% Lauric acid	42		115		190	
39	Unst. PP + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	42		115		190	

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Table 3 continued

Ex. No.	Composition	88°C Hrs.	60°C Hrs.	49°C Hrs.
40	5A95 PP + 50ppm Mn + 2% Linseed oil + Stearic acid	42	195	195
41	6-166 PP/PE + 50ppm Mn + 4% Oleic acid	65	120	195
42	5A95 PP + 50ppm V + 2% Linseed oil + 2% Stearic acid	65	195	190
43	5A95 PP + 50ppm Mn + 2% Tung Oil + 2% Stearic acid	65	260	595
44	7C50 PP/PE + 50ppm Mn + 4% Oleic acid	88	115	195
45	7C50 PP/PE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	88	165	285
46	Unstabilized 5A95 PP powder (100%)	88	326	400
47	6180 HDPE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	96	235	475
48	5A95 PP + 50ppm Fe + 2% Linseed oil + 2% Stearic acid	110	650	>700
49	1550P LDPE/5A95 PP(77/19) + 50ppm Mn + 4% Oleic acid	134	231	310
50	5A95 PP + 50ppm Ce + 2% Linseed oil + 2% Stearic acid	260	400	>700

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Table 3 continued

Ex. No.	Composition	88°C Hrs.	60°C Hrs.	49°C Hrs.
51	1550P LDPE/5A95 PP(77/19) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	260	550	>700
52	1550P LDPE + 50ppm Mn + 4% Oleic acid	260	>700	>700
53	1550P LDPE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	305	>700	>700
54	6180 HDPE + 50ppm Mn + 4% Oleic acid	400	>700	>700
55	5A95 PP + 50ppm Mn + 2% Coconut oil + 2% Stearic acid	405	>700	>700
56	5A95 PP + 50ppm Ce + 4% Oleic acid	455	>700	400
57	5A95 PP + 50ppm V + 4% Oleic acid	545	>700	>700
58	6-166 PP/PE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	575	350	>700
59	5A95 PP + 50ppm Mn + 4% β -methylcinnamic acid	>700	>700	>700
60	5A95 PP + 50ppm Mn + 4% Lauric acid	>700	>700	>700
61	5A95PP + 50 ppm Fe + 4% Oleic acid	>700	>700	>700
62	5A95 PP + 50ppm Mn + 4% Stearic acid	>700	>700	>700

1 5A95 is Shell 5A95. 2 Unstabilized PP is a 9.0 MFI material available from Shell.

3 7C50 PP/PE is Shell 7C50, 8.0 MFI and 8% PE. 4 6180 HDPE is NHD 6180 available from Quantum Co., Rolling Meadows, IL with an MI of 1.15 and a density of 0.960.

5 1550P LDPE is Tenite™, 3.5 MFI and 8.0 MFI. 6 6-166 PP/PE is random copolymer available from Shell, and 0.9 density, available from Eastman Chemical Products, Kingsport, TN.

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Samples from Examples 29-62 were stored at room temperature for approximately 1900 hours and checked for embrittlement. Examples 29-41 film samples showed evidence of embrittlement, while Examples 42-62 5 film samples showed no signs of embrittlement.

Table 4 shows the embrittlement time for Examples 29-62 film samples in a dry oven.

TABLE 4

Ex. No.	Composition	88°C Hrs.	70° Hrs.	60°C Hrs.	49°C Hrs.
29	5A95 PP + 50ppm Co + 4% Oleic acid	2	3	9	16
30	Unst. PP + 50ppm Mn + 4% Oleic acid	1	3	7	18
31	Unst. PP + 50ppm Fe + 4% Oleic acid	3.5	11	33	72
32	5A95 PP + 50ppm Co + 2% Linseed oil + 2% Stearic acid	2	9	30	72
33	Unst. PP + 50ppm Fe + 2% Linseed oil + 2% Stearic acid	4.5	24	85	221
34	5A95 PP + 50ppm Mn + 4% Oleic acid	2	7	20	48
35	Unst. PP + 50ppm Fe + 4% Stearic acid	6	18	60	143
36	5A95 PP + 50ppm Mn + 4% Linoleic acid	1.5	5	16	40
37	5A95 PP + 50ppm Mn + 2% Linseed oil + 2% Oleic acid	2	8	30	54
38	5A95 PP + 50ppm Mn + 2% Linseed oil + 2% Lauric acid	2	7	20	55
39	Unst. PP + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	3	9.5	36	94
40	5A95 PP + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	2	6	25	54
41	6-166 PP/PE + 50ppm Mn + 4% Oleic acid	6	22	46	97
42	5A95 PP + 50ppm V + 2% Linseed oil + 2% Stearic acid	17	84	335	>800
43	5A95 PP + 50ppm Mn + 2% Tung Oil + 2% Stearic acid	2.5	9	30	90
44	7C50 PP/PE + 50ppm Mn + 4% Oleic acid	3.5	12	37	76
45	7C50 PP/PE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	3	10	36	76
46	Unstabilized 5A95 PP powder (100%)	22.5	108	385	>800

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47	6180 HDPE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	8	34	120	294
48	5A95 PP + 50ppm Fe + 2% Linseed oil + 2% Stearic acid	53	235	>800	>800
49	1550P LDPE/5A95 PP(77/19) + 50ppm Mn + 4% Oleic acid	12.5	69	284	294
50	5A95 PP + 50 ppm Ce + 2% Linseed oil + 2% Stearic acid	7	34	130	294
51	1550P LDPE/5A95 PP(77/19) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	25.5	114	212	433
52	1550P LDPE + 50ppm Mn + 4% Oleic acid	82	290	60	>800
53	1550P LDPE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	82	470	740	>800
54	6180 HDPE + 50ppm Mn + 4% Oleic acid	22	47	120	221
55	5A95 PP + 50ppm Mn + 2% Coconut oil + 2% Stearic acid	3	16	62	150
56	5A95 PP + 50ppm Ce + 4% Oleic acid	22	24	60	97
57	5A95 PP + 50ppm V + 4% Oleic acid	22.5	90	165	294
58	6-166 PP/PE + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	4.5	13	51	94
59	5A95 PP + 50ppm Mn + 4% β -methylcinnamic acid	11.5	185	240	>800
60	5A95 PP + 50ppm Mn + 4% Lauric acid	4	18	62	200
61	5A95 PP + 50ppm Fe + 4% Oleic acid	31.5	145	335	605
62	5A95 PP + 50ppm Mn + 4% Stearic acid	7	41	140	480

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Examples 63-79

Samples were prepared using various polypropylenes (unstabilized and stabilized commercial 5 polymers), stabilized polyethylenes and stabilized blends thereof, as defined in Table 3, using the procedure outlined above. Samples were then placed in water jars and buffered to a pH of 6 using a phosphate 10 buffer. The samples were tested for embrittlement as described above for Examples 1-14 except for the polyethylenes and blends which were tested for softness and loss of tensile strength. The time for embrittlement is shown in Table 5 below. The samples were tested soon after extrusion.

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TABLE 5

Ex. No.	Composition	88°C Hrs.	60°C Hrs.	49°C Hrs.
63	5A95 PP + 50ppm Mn + 4% Erucic acid	42	120	185
64	5A95 PP + 50ppm Mn + 4% Linseed oil + 2% Euric acid	42	113	190
65	5A95 PP + 50ppm Mn + 4% Oleic acid	45	120	210
66	Unst. PP + 50ppm Mn + 4% Oleic acid + 600ppm Irg. 1010	70	190	210
67	Unst. PP + 50ppm Fe + 4% Oleic acid + 600ppm Irg. 1010	70	190	330
68	5A95 PP + 50ppm Mn + 2% Linseed oil + 2% Linolenic acid	95	210	355
69	5A95 PP + 50ppm Mn + 4% Linseed oil	95	190	355
70	5A95 PP + 50ppm Mn + 4% Linolenic acid	165	230	240
71	1550P LDPE/5A95 PP (66:30) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	165	360	>350
72	1550P LDPE/5A95 PP (66:30) + 50ppm Mn + 4% Oleic acid	190	>350	360
73	1550P LDPE/5A95 PP (76:20) + 50ppm Mn + 4% Oleic acid	210	240	>350
74	1550P LDPE/5A95 PP (86:10) + 50ppm Mn + 4% Oleic acid	210	360	>350
75	1550P LDPE/5A95 PP (76:20) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	220	>350	>350
76	1550P LDPE/5A95 PP (86:10) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	230	>350	>350
77	5A95 PP + 4% Oleic acid	355	210	360

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78	5A95 PP + 50ppm Mn + 4% Tung Oil	360	>350	>350
79	5A95 PP + 50ppm Mn + 4% Coconut Oil	>350	>350	>350

1 Irganox 1010 is a hindered phenol available from Ciba-Geigy Co.

Table 6 shows the embrittlement time for Examples 63-79 film samples in a dry oven.

TABLE 6

Ex. No.	Composition	88°C Hrs.	70°C Hrs.	60°C Hrs.	49°C Hrs.
63	5A95 PP + 50ppm Mn + 4% Erucic acid	3	7.5	25	55
64	5A95 PP + 50ppm Mn + 2% Linseed oil + 2% Erucic acid	2	7	28	58
65	5A95 PP + 50ppm Mn + 4% Oleic acid	2	6	21	52
66	Unst. PP + 50 ppm Mn + 4% Oleic acid + 600 Irg. 1010	3.75	7.5	26	55
67	Unst. PP + 50 ppm Fe + 4% Oleic acid + 600 Irg. 1010	23	33	80	123
68	5A95 PP + 50 ppm Mn + 2% Linseed oil + 2% Linolenic acid	2.5	8	26	65
69	5A95 PP + 50ppm Mn + 4% Linseed oil	3.5	10	34	65
70	5A95 PP + 50ppm Mn + 4% Linolenic acid	2.5	7	23	55
71	1550P LDPE/5A95 PP (66:30) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	20	33	315	244
72	1550P LDPE/5A95 PP (66:30) + 50ppm Mn + 4% Oleic acid	9.5	33	130	148
73	1550P LDPE/5A95 PP (76:20) 50ppm Mn + 4% Oleic acid	27	100	267	225
74	1550P LDPE/5A95 PP (86:10) + 50ppm Mn + 4% Oleic acid	50	172	320	560
75	1550P LDPE/5A95 PP (76:20) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	27	123	219	267
76	1550P LDPE/5A95 PP (86:10) + 50ppm Mn + 2% Linseed oil + 2% Stearic acid	50	130	130	>560
77	5A95 PP + 4% Oleic acid	25.5	90	95	155
78	5A95 PP + 50ppm Mn + 4% Tung Oil	3	16	58	123
79	5A95 PP + 50ppm Mn + 4% Coconut Oil	6	27	99	155

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Examples 80-94

These films, 4 mil caliper, (100 micrometers) were prepared in accordance with Examples 1-14 with the exception of Examples 83-89 which were 1 mil films (25 micrometers). The compositions included various naturally biodegradable polymers (Tone™ P-700 and Tone™ 767P are poly-ε-caprolactones (PCL) available from Union Carbide of Danbury, CT; Bipol™ PHBV is a poly(hydroxybutyrate valerate) (12% valerate) available from ICI Americas, Inc.; Vinex™ 2025 and 2025U are polyethylene/vinyl-alcohol copolymers available from Air Products & Chemicals, Inc. of Allentown, PA; Elvax™ 260 is an ethylene/vinyl acetate copolymer (EVA) (28% vinyl acetate and 6 MFI) available from DuPont Co., Wilmington DE; Nucrel™ 960 is a polyethylene/methylacrylate copolymer (density = 0.94, MFI = 60) available from DuPont Co. The poly-L-lactide has an intrinsic viscosity of 1.04 and is available from Birmingham Polymers, Inc. The polyesteramide - 10,2 (PEA) has an instrinsic viscosity of 0.7 and is available from 3M Company, St. Paul, MN, and Pamolyn™ 100 (PAM) is an oleic acid (91%) available from Hercules, Inc., Wilmington, DE).

Films from Examples 81 and 82 were tested for degradation in water and air, as described above, at 60°C. The Example 81 films became embrittled at 43 hours in air and 112 hours in water. The Example 82 films became embrittled at 53 hours in air and 332 hours in water. The times to embrittlement in air for Examples 83-94 are given in Table 7 below.

TABLE 7

Ex. No.	Composition	88°C Hrs.	70°C Hrs.	60°C Hrs.	49°C Hrs.
83	3% POLY-L-LACTIDE + 2% PAM 100	72	465	850	>850
84	6% POLY-L-LACTIDE + 2% PAM 100	152	370	>850	>850
85	9% POLY-L-LACTIDE + 2% PAM 100	80	320	750	>850
86	9% PEA-10,2 + 2% PAM 100	63	365	>850	>850
87	5% PCL + 20% 7C50 + 2% PAM 100	50	130	290	750
88	5% VINEX 2025U PVA + 20% 7C50 + 2.5% ELVAX 260 EVA + 2% PAM 100	50	76	225	>850
89	5% PHBV (12% V) + 20% 7C50 + 2.5% ELVAX 260 EVA + 2% PAM 100	50	225	490	>850
90	20% P700 + 2% PAM 100	6	24	52	100
91	20% 2025 PVA + 2% PAM 100	60	155	245	370
92	20% PVA + 10% NUCREL 960 + 2% PAM 100	50	175	325	465
93	20% PVA + 10% ELVAX 260 + 2% PAM 100	225	175	290	465
94	20% PHBV + 10% ELVAX 260 + 2% PAM 100	---	---	---	---

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Examples 80-82

5	80)	Shell 5A95	88.94%
		Tone P-700	10.00%
		Tung Oil	1.00%
		Manganese (Mn) Stearate	0.06%
10	81)	Shell 5A95	85.94%
		Tone 767P	10.00%
		Pamolyn™ 100	4.00%
		MnStearate	0.06%
15	82)	Shell 5A95	85.94%
		Bipol™ PHBV	10.00%
		Pamolyn™ 100	4.00%
		MnStearate	0.06%

20 Example 82 was of poor quality because of the incompatibility of PHBV with polyolefins.

Examples 83-89 (1 mil LDPE Films)

25	83)	Tenite™ 1550P	94.94%
		poly-L-lactide	3.00%
		Pamolyn™ 100	2.00%
		MnStearate	0.06%
30	84)	Tenite™ 1550P	91.94%
		poly-L-lactide	6.00%
		Pamolyn™ 100	2.00%
		MnStearate	0.06%
35	85)	Tenite™ 1550P	88.94%
		poly-L-lactide	9.00%
		Pamolyn™ 100	2.00%
		MnStearate	0.06%
40	86)	Tenite™ 1550P	88.94%
		polyesteramide-10,2	9.00%
		Pamolyn™ 100	2.00%
		MnStearate	0.06%
45	87)	Tenite™ 1550P	72.94%
		Tone P-700	5.00%
		Shell 7C50 PP/PE copolymer	20.00%
		Pamolyn™ 100	2.00%
		MnStearate	0.06%

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88)	Tenite™ 1550P	72.94%
	Vinex™ 2025U	5.00%
	Shell 7C50 PP/PE	17.50%
	Elvax™ 260	2.50%
5	Pamolyn™ 100	2.00%
	MnStearate	0.06%
89)	Tenite™ 1550P	72.94%
	Bipol™ PHBV	5.00%
10	Shell 7C50	17.50%
	Elvax™ 260	2.50%
	Pamolyn™ 100	2.00%
	MnStearate	0.06%
15	<u>Examples 90-04 (4 mil PP/PE copolymer films)</u>	
90)	Shell 7C50	78.35%
	Tone™ P-700	19.59%
	Pamolyn™ 100	2.00%
20	MnStearate	0.06%
91)	Shell 7C50	78.35%
	Vinex™ 2025	19.59%
	Pamolyn™ 100	2.00%
25	MnStearate	0.06%
92)	Shell 7C50	68.56%
	Vinex™ 2025	19.59%
	Nucrel™ 960	9.79%
30	Pamolyn™ 100	2.00%
	MnStearate	0.06%
93)	Shell 7C50	68.50%
	Vinex™ 2025U	19.59%
35	Elvax™ 260	9.79%
	Pamolyn™ 100	2.00%
	MnStearate	0.06%
94)	Shell 7C50	82.95%
40	Bipol™ PHBV	10.00%
	Elvax™ 260	5.00%
	Pamolyn™ 100	2.00%
	MnStearate	0.06%
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Examples 95-98

Films were prepared and tested as described above for Examples 1-14, using unstabilized polypropylene with 2% added Pamolyn™ 100 and 400 ppm Fe (as Fe Stearate) at various levels of Irganox™ 1010. The films were tested for embrittlement at various temperatures as indicated in Table 8 below.

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TABLE 8

Example	Irganox™ (PPM)	88°C Hrs.	70°C Hrs.	60°C Hrs.	49°C Hrs.
95	0	4	13	40	96
96	200	7.5	34	96	215
97	600	20	80	260	650
98	1000	39	215	1500	_____

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The films were also kept on a shelf at room temperature for approximately 3,900 hours and tested for embrittlement. The Examples 95 and 96 films had embrittled at this time, but the Examples 97 and 98 films had not.

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Examples 99-101

Immature compost was allowed to dry until it contained only 5% water. To 1000 g of this compost were added 200 g of dried, shredded maple leaves, 6 g of Compost Plus (Ringer Corporation, Minneapolis, MN) and sufficient water to yield of mixture of 54% water. The compost mixture was placed in a wire mesh basket in a Nalgene tank (Nylon - 14"x10"x10" from Fisher) in a forced air oven at 50°C. The compost was aerated from

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the bottom by suspending the wire basket over two glass frits (10"x1.5") in a pool of water through which air was bubbled. The compost mixture containing the film sample was piled in the wire basket so that the samples were completely covered. Several samples could be tested in one such apparatus.

The test period was one month. The initial carbon-to-nitrogen ratio of the compost mixture was 40:1. The pH of the system remained relatively neutral, ranging from 5.5-7.0. Moisture was maintained at 45-55% by adding water as necessary. The compost was manually turned daily and film samples were checked for embrittlement. Embrittlement was not as pronounced in the simulated compost test as it was in the dry oven tests however roughly correlated to the water jar test results. Films usually tore first in one direction, and then both, before becoming brittle. Embrittlement times for Examples 99-101 are listed in Table 9 below.

TABLE 9

<u>Example</u>	<u>Film</u>	<u>Compost 50°C</u>
99	5A95PP + 50ppm Co + 4% Oleic Acid	10 days
100	Unstab. 5A95PP + 50ppm Mn + 4% Oleic acid	27 days
101	5A95PP/Tone™ 767P PCL (9:1) + 50 ppm Mn + 4% Oleic Acid	26 days

The various modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention, and this invention should not be restricted to that set forth herein for illustrative purposes.

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We claim:

1. An extrudable compostable polymer composition comprised of an extrudable thermoplastic polymer, copolymer or blends containing a prodegradant system of
5 an auto-oxidative component and a transition metal characterized in that the auto-oxidative component comprises a fatty acid, a substituted fatty acid or derivatives, or blends thereof, the fatty acid having
10 being at between about 0.1 to 10 weight percent based on the total composition wherein the auto-oxidative component provides at least 0.1 weight percent of unsaturated species and at least 0.1 weight percent of free acid species in the total composition, and from 5
15 to 500 ppm of a transition metal in the form of a salt wherein the transition metal is selected from cobalt, manganese, copper, cerium, vanadium and iron.
2. A film formed from the polymer composition of
20 claim 1.
3. The polymer composition of claims 1 and 2 wherein the auto-oxidative component comprises an unsaturated fatty acid.
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4. The polymer composition of any of claims 1-3 wherein the transition metal salt comprises a transition metal salt having an organic ligand.
- 30 5. The polymer composition of any of claims 1-3 wherein the auto-oxidative component comprises an admixture of saturated fatty acids and unsaturated fatty acid esters.
- 35 6. The polymer composition of any of claims 3-5 wherein the unsaturated fatty acid substantially comprises species having two or more double bonds.

7. The polymer composition of any of claims 1-6 wherein the composition in the form of a film of about 100 microns will oxidatively degrade to embrittlement within 14 days at 60°C and a relative humidity of at least 80%.

8. The polymer composition of any of claims 1-7 wherein the transition metal salt is present at a concentration of less than 200 parts per million.

9. The polymer composition of any of claims 1-8 further comprising an anti-oxidant at a concentration of from about 0.02 to 0.2 weight percent.

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10. The polymer composition of any of claims 1-9 further comprising a naturally biodegradable thermoplastic polymer at a concentration of from about 5 to 50 weight percent.

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11. The polymer composition of any of claims 1-10 wherein the extrudable thermoplastic polymer comprises a polyolefin polymer, copolymer or blend.

12. The polymer composition of claim 11 wherein the polyolefin comprises polypropylene or polyethylene.

13. The polymer composition of any of claims 1-12 wherein the auto-oxidative component comprises at least 0.5 weight percent of the composition.

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14. The polymer composition of any of claims 1-13 further comprising 5 to 25 weight percent of a naturally biodegradable polymer.

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15. The polymer composition of any of claims 1-14 wherein the naturally biodegradable polymer is selected

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from the group consisting of poly(caprolactone),
poly(lactic acid), poly(hydroxybutyrate-valerate),
poly(ethylene adipate), poly(vinyl alcohol), modified
starch/olefin copolymers, poly(propylene oxide), and
5 poly(ethylene oxide).

16. The polymer composition of any of claims 1-15
wherein the transition metal is selected from the group
consisting of cobalt, manganese, copper and cerium.

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17. The polymer composition of claim 7 wherein
the composition will oxidatively degrade to
embrittlement within 14 days at 60°C and a relative
humidity of at least 80% when tested after a stable
15 shelf life of from about 1 week to 12 months.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/10717

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08K5/09; C08K5/10		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US,A,3 840 512 (D.S. BRACKMAN) 8 October 1974 cited in the application see the whole document ---	1-4,7-9, 11-13, 16,17
Y	US,A,4 067 836 (J.E. POTTS ET AL) 10 January 1978 cited in the application see column 3, line 60 - column 9, line 47; claims ---	1-4,7-9, 11-13, 16,17
A	US,A,3 921 333 (CLENDINNING ET AL) 25 November 1975 cited in the application see claims -----	1,10,14, 15
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15 FEBRUARY 1993	25.02.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DE JONGE S.J.P.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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