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(21) International Application Number: PCT/US91/09731 (22) International Filing Date: 20 December 1991 (20.12.91) (30) Priority data: 632,362 21 December 1990 (21.12.90) US (71) Applicant: ECOSTAR INTERNATIONAL L.P. [US/US]; 181 Cooper Street, Tonawanda, NY 14150-6645 (US). (72) Inventors: CHAPMAN, Graham, M. ; Withyditch Cottage, Summer Lane, Combe Down, Bath, Avon BA2 7ER (GB). DOWNIE, Robert, H. ; 210 Rollingwood, Willi- amsville, NY 14221 (US). (74) Agents: LINIHAN, Martin, G. et al.; 1800 One M & T Pla- za, Buffalo, NY 14203 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: PHOTODEGRADABLE PLASTIC COMPOSITION (57) Abstract A thermoplastic composition is provided which is degradable under the action of sunlight and/or ultraviolet light. The thermoplastic composition comprises a thermoplastic polymer, a first transition metal compound which may be a complex, a second transition metal compound and an aromatic ketone. The thermoplastic polymer preferably comprises an olefin such as polyethylene, ethylene copolymers, polypropylene, polystyrene or polyurethane. The first transition metal compound preferably comprises an iron compound such as iron stearate. The second transition metal preferably comprises copper stearate and the aromatic ketone preferably comprises benzophenone.		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

PHOTODEGRADABLE PLASTIC COMPOSITIONFIELD OF THE INVENTION

This invention relates generally to plastic compositions, and more particularly, to a thermoplastic composition which comprises a thermoplastic polymer such as polyethylene or ethylene copolymers, polypropylene, polystyrene or polyurethane which is photodegradable when exposed to sunlight and/or ultraviolet light.

BACKGROUND OF THE INVENTION

Plastic waste is normally disposed of by recycling, incineration or burying in a landfill. Unfortunately, some materials are improperly disposed of and become litter. This litter is both esthetically objectionable and poses a threat to wildlife through possible entrapment and/or ingestion. Therefore, there is a need for a material which will degrade harmlessly when exposed to sunlight, ultraviolet light or heat.

There are known additive compositions which may be incorporated into thermoplastic materials to enhance degradation of the plastic. For example, U.S. patent 4,931,488 discloses a thermoplastic polymer composition to which has been added a biologically degradable substance such as starch, an iron compound, an oxidizable substance selected from fatty acids and/or fatty acid esters and a transition metal. This composition demonstrates biodegradation and photodegradation capability when exposed to heat, ultraviolet light, sunlight, or under composting conditions. But, many states

today require only that a plastic composition only be photodegradable. In this connection, the use of a composition such as that disclosed in patent 4,931,488 may not be advantageous. The starch component in the composition becomes unnecessary when biodegradation is not required, and the starch may cause the product to become sensitive to moisture pickup during the production process and does little to enhance photodegradation.

Therefore, a plastic composition which possesses the desired properties of thermoplastic materials, yet readily degrades when exposed to sunlight and/or ultraviolet light, is highly desirable.

SUMMARY AND OBJECTS OF THE INVENTION

Accordingly, it is the primary object of the present invention to provide a plastic composition which readily degrades when exposed to sunlight and/or ultraviolet light and to provide such a plastic composition for films, sheets or other moldings, which possesses the desired properties of known thermoplastic materials.

In accordance with the present invention, there is provided a thermoplastic composition which is degradable under the action of sunlight and/or ultraviolet light and heat. The thermoplastic composition comprises a thermoplastic polymer, a first transition metal compound which may be a complex, a second transition metal compound and an aromatic ketone.

More particularly, the thermoplastic polymer preferably comprises an olefin such as polyethylene, ethylene copolymers, polypropylene, polystyrene or polyurethane. The first transition metal comprises an iron compound such as ferric hydroxy stearate,

which is soluble in the composition and acts as an initiator which promotes further degradation. The second transition metal comprises a copper compound which acts as a catalyst with the iron compound to enhance degradation. The aromatic ketone includes benzophenone. It has been found that by using the composition of the present invention in a thermoplastic material that a significant synergistic degradation effect occurs on the plastic when exposed to sunlight and/or ultraviolet light.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph illustrating loss of elongation at break as a function of time in a plastic film product including the composition of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic composition in accordance with the present invention facilitates biodegradation of thermoplastic materials under the action of sunlight and/or ultraviolet light and heat. That is, the chemicals in the composition in the presence of the sunlight or ultraviolet light and heat react to form free radicals which break the bonds of the thermoplastic polymer resulting in a reduction of molecular weight and loss of physical properties. Thereafter, the thermoplastic material becomes weak and brittle which results in a material that is easily disintegrated by exposure to the elements.

The thermoplastic composition of the present invention comprises as one component thereof a thermoplastic base of any known thermoplastic polymer and preferably polymers of olefins such as

polyethylene, ethylene copolymers, polypopylene, polystyrene or polyurethane. "Polyethylene" as used herein, comprises any type of polyethylene, such as LDPE, LLDPE, LMDPE, MDPE, HDPE, ULDPE, etc. Examples of suitable ethylene copolymers include EVA, EBA, EAS, EMAA and ionomers. It is understood that the composition of the present invention may be formed in any of the following manners. The composition may be added directly at the final production stage by the manufacturer, formed in a concentrate and supplied to the manufacturer to be added to the base resin or formed with the base resin and supplied to the manufacturer ready for use.

The first transition metal component preferably comprises an iron compound generally having the formula $X-Fe$, where X represents one or more ligands. The compound may additionally be coupled to a further ligand Y . Fe may designate iron in any known valancy. The ligand X may be an inorganic or organic acid radical or likewise another ligand bonded in a complex. For purposes of illustration, examples of suitable ligands X include OH^- , Cl^- , Br^- , I^- , oxalate-, H -citrate-, NO_2^- , N_3^- EDTA or a carbonyl, nitrosyl or porphyrin radical. Examples of suitable ligands Y include carboxylic acid ions of aromatic or aliphatic monocarboxylic acid or of dicarboxylic acids, the aliphatic carboxylic acid preferably having 10 to 20 carbon atoms. Ligand Y serves in general to increase the solubility of the compound $X-Fe$ in the polymer. The iron compound more preferably is comprised of iron stearate present in the final concentration of the present invention in an amount from about 0.01 weight percent to about 0.5 weight percent, and more preferably in an amount from about 0.1 weight percent to about 0.3

weight percent. It is understood that the ranges listed herein are for purposes of illustration. The amount listed for the upper limits is based on economics, and therefore, the components may be present in the concentration in amounts greater than those listed. Although, a saturation limit is reached at which further addition does not provide greater effectiveness. The minimum value listed provides minimum measurable improvements in photodegradation.

The second transition metal compound of the thermoplastic composition of the present invention acts as a catalyst with the first transition compound to enhance degradation of the thermoplastic material. The compound may comprise a complex having the general formula $Z'-Me$, wherein Me designates a transition metal other than iron if iron is the first transition metal and Z' designates one or more ligands. For purposes of illustration only and, not limitation, examples of ligands include OH^- , Cl^- , Br^- , I^- , oxalate-, H-citrate-, NO_2^- , N_3^- , EDTA, as well as carboxylic acid ions of aromatic or aliphatic monocarboxylic or dicarboxylic acids, the aliphatic carboxylic acid preferably having 10 to 20 carbon atoms. The preferred transition metals comprising Me are the transition metals of the first transition metal row in the periodic table, and more preferably copper and vanadium. The most preferred second transition metal compound is copper stearate present in the final concentrate of the present invention in an amount from about 0.005 weight percent to about 0.1 weight percent, and more preferably cupric stearate in an amount from about 0.01 weight percent to about 0.06 weight percent.

The aromatic ketone component of the composition of the present invention has been found to have

a synergistic effect that speeds up the photodegradation of the thermoplastic. This is an unobvious finding since aromatic ketones generally are ultraviolet stabilizers. For purposes of illustration only and, not limitation, examples of aromatic ketones include benzophenone, anthraquinone, anthrone or derivatives such as acetylbenzophenone or 4-octyl benzophenone.

The more preferred aromatic ketone is benzophenone which is present in the concentration in an amount of from about 0.01 weight percent to about 0.7 weight percent and more preferably in an amount from about about 0.02 weight percent to about 0.15 weight percent.

Utilizing the composition of the present invention is further advantageous in that the degradation can be controlled depending on the field of application by varying the concentration of the individual components, without the plastic material suffering a deterioration in its properties under normal use conditions. Particular fields of application of the composition of the present invention include packaging materials, films for garbage bags for compostable wastes, agricultural films, and in particular those materials which may become litter such as disposable packaging. Furthermore, the present invention makes it possible to manufacture products which do not pollute the environment and which can be degraded without additional energy consumption and without releasing harmful substances.

The production of the thermoplastic composition in a concentrate form in accordance with the present invention and its processing to give sheets, films, plates or other shapes is carried out by any conventional method. For example, the polyethylene may be

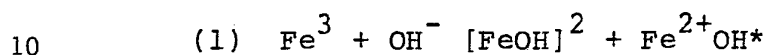
combined with the appropriate amounts of iron stearate, copper stearate and benzophenone in a twin screw compounding extruder or equivalent and extruded and pelletized into a concentrate or masterbatch. Extruded film, blow molded parts or injection moulded parts are made by combining this concentrate with polyethylene or other base resins in a film extruder or injection molding extruder, which is normally of the single screw type.

As an alternative the chemicals could be added directly at the final production stage in the single screw extruder, this however is not very practical. This technique would require either a premixing step or a number of additional additive feeders on the extrusion machine. In addition, single screw extruders are typically poor mixing devices. By producing a concentrate first the active ingredients are predispersed in the thermoplastic base i.e., polyethylene, making the final dispersal in the single screw machine much easier.

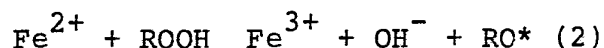
The degradation process appears to proceed according to the following mechanism, with reference to A.C. Albertsson, B. Randy, J. Appln. Polym. Sci Appl. Polym Symp., 35 (1979) p. 423 and the publication of A.C. Albertsson mentioned therein, which is hereby incorporated by reference.

Plastics with C-C bonds in the main chain biodegrade extremely slow with the formation of CO_2 and H_2O . The half life of biological degradation of polyethylene was extrapolated to be at least 100 years. Under the action of ultraviolet light, sunlight or heat free radicals such as, for example OH^* are formed due to the presence of iron ions, and these can react with the polymers forming other free radicals. These free polymer radicals are extremely

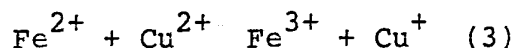
reactive and can, inter alia, react further with oxygen, other chains, iron ions, and the like. Polymer chains are thus split and small chains with or without oxygen-containing groups, such as alcohols, ketones, etc. are formed. During this process, iron ions act both as an initiator and as a reaction promoter since iron-(III) hydroxide complexes are highly reactive. This can be illustrated the by the following equation:



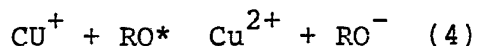
The observed catalytic effect of the transition metal compounds, copper or vanadium compounds, is probably attributed to an acceleration of the $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ cycle. Without these compounds, the Fe^{2+} formed according to equation (1) may be reoxidized by other free radicals or other intermediates at the expense of chain splitting as for example, shown in the following equation:



In the presence of copper compounds, the Fe^{2+} formed is reoxidized faster according to the following equation:



and Cu^+ ions are reoxidized very fast to Cu^{2+} ions by free radicals as follows:



This process repeats itself as long as the polymer is exposed to ultraviolet light, sunlight or heat. In this phase, the plastic materials become brittle and fragile and disintegrate into small

particles of about a few mm² up to about a few cm². Depending on the prevailing conditions, this phase takes in general from about 10 to 60 days.

5 The following table sets forth a preferred formulation for the thermoplastic composition of the present invention formed in a concentrate wherein the compositional ranges of the various components are by weight percent of the total concentrate.

TABLE A

- 10 a. From about 0.01 percent to about 0.5 percent first transition metal compound;
b. From about 0.005 percent to about 0.1 percent second transition metal compound;
15 c. From about 0.01 percent to about 0.2 percent aromatic ketone;
d. Balance thermoplastic polymer.

The following table sets forth a more preferred formulation for the thermoplastic composition of the present invention formed in a concentrate wherein
20 the compositional ranges of the various components are by weight percent of the total concentrate.

TABLE B

- a. From about 0.1 percent to about 0.3 percent iron stearate;
25 b. From about 0.01 percent to about 0.06 percent copper stearate;
c. From about .02 percent to about 0.15 percent benzophenone;
d. Balance thermoplastic polymer.

30 The following tables set forth a still more preferred formulation for the thermoplastic

composition of the present invention formed in a concentrate wherein the compositional ranges of the various components are by weight percent of the total concentrate.

TABLE C

5

- a. About 0.124 percent ferric 12 hydroxy stearate;
- b. About 0.024 percent cupric stearate;
- c. About 0.052 percent benzophenone;
- 10 d. Balance thermoplastic polymer.

TABLE D

15

- a. About 0.31 percent ferric 12 hydroxy stearate;
- b. About 0.06 percent cupric stearate;
- c. About 0.13 percent benzophenone;
- d. Balance thermoplastic polymer.

With reference to Figure 1, there is shown loss of elongation at break using a film product to which the composition of the present invention has been added, and a control comprised of polyethylene without the additive composition. The film product indicated by Formulation 1 in Figure 1 has the composition of Table C added thereto. The film product indicated by formulation 2 in Figure 1 has the composition of Table D added thereto. The control film, Formulations 1 and 2 were exposed in a "QUV" weatherometer, a testing device which uses ultraviolet light and moisture to simulate outdoor exposure. It is apparent from Figure 1 that films comprised with the composition of the present invention photodegrade at a much faster rate than the control film without the composition of the present invention.

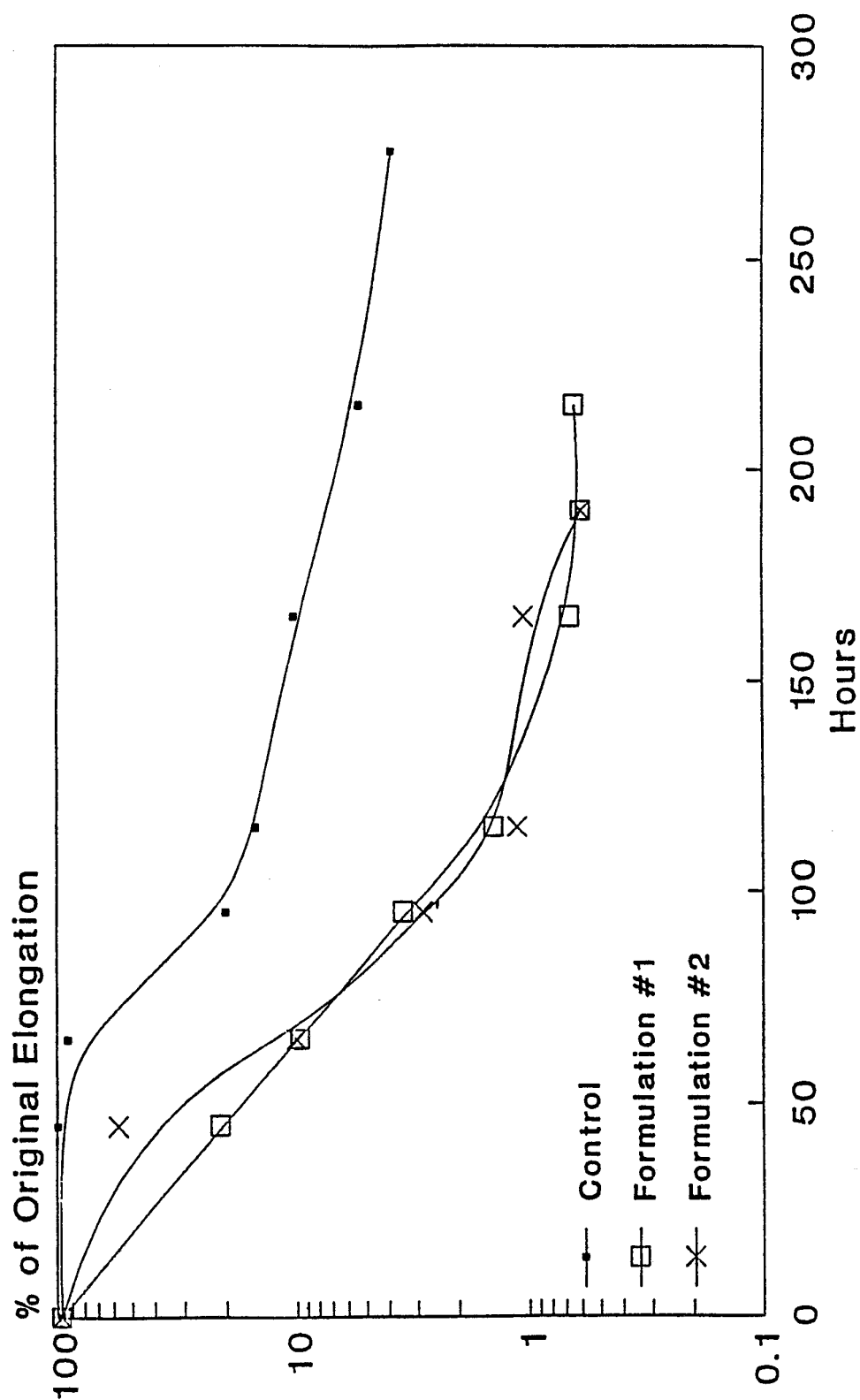
It will be understood that the foregoing description and illustration is by way of example only and that such modifications and changes as may suggest themselves to those skilled in the art are
5 intended to fall within the scope of the present invention.

What is claimed is:

CLAIMS:

1. A thermoplastic composition which is degradable under the action of heat, ultraviolet light and/or sunlight and which comprises as a polymeric compound thermoplastic polymers of olefins comprising
5 polyethylene, ethylene copolymers, polypropylene, polystyrene or polyurethane characterized in that the composition contains the following degradation-promoting additives:
 - 10 a) a first transition metal compound which is soluble in the composition and which acts as an initiator and promotes further degradation;
 - b) a second transition metal compound which acts as a catalyst with the first transition
15 metal compound to enhance said degradation; and
 - c) an aromatic ketone.
2. The thermoplastic composition of claim 1,
wherein said first transition metal compound is iron
20 stearate present in the composition in an amount of from about 0.1 wt.% to about 0.5 wt.%.
3. The thermoplastic composition of claim 2,
wherein said second transition metal compound is copper stearate present in the composition in an
25 amount of from about 0.005 wt.% to about 0.1 wt.%.
4. The thermoplastic composition of claim 3,
wherein said aromatic ketone is benzophenone.
5. The thermoplastic composition of claim 4,
wherein said benzophenone is present in the composition
30 in an amount of from about 0.01 wt.% to about 0.2 wt.%.

Loss of Elongation at Break Photodegradable Formulations



Exposure in Q-Panel

Fig. 1.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 91/09731

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (5): C08F 8/50		
U.S. CL. 523/124, 125, 126; 524/359, 398		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
U.S.	523/124, 125, 126; 524/359, 398	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁶
X	US, A, 3,941,759 (TAYLOR ET AL.) 02 MARCH 1976; See entire document.	1-5
X	US, A, 3,981,856 (HUDGIN ET AL.) 21 SEPTEMBER 1976; See entire document.	1-5
X	US, A, 4,495,315 (MIYOSHI ET AL.) 22 JANUARY 1985; See entire document.	1-5
X	US, A, 4,517,318 (MIYOSHI ET AL.) 14 MAY 1985; See entire document.	1-5
* Special categories of cited documents: ¹³ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered 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. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ³
12 FEBRUARY 1992		02 MAR 1992
International Searching Authority ¹		Signature of Authorized Officer ¹⁰
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