



425-201-A
4794/05341
07/485224 1/29/90

ENHANCED DEGRADATION OF THERMOPLASTICS

Background of the Invention

Thermoplastics are ever-present as components of
5 packaging, containers, disposable diapers, and other short-term
applications. Unfortunately, the large quantities of the waste
products containing these materials generated by consumers and
commercial establishments such as fast food stores must be
disposed of. The persistence of these plastic wastes consumes
10 increasingly precious landfill space and much of the waste washed
up on beaches is plastic.

Brief Description of the Invention

It has now been found that (certain) organic titanium and
zirconium pyrophosphate derivatives substantially reduce the
15 persistence of plastics, particularly of the types normally
associated with landfill systems and ocean dumping, thereby
helping to alleviate this growing problem. Specifically, it has
been found that the post-use or preformulation addition of
certain alkali-soluble organo-metallic quaternary pyrophosphates
20 significantly accelerates the environmental degradation of a
variety of thermoplastic articles under simulated landfill
conditions. In addition, it has been found that (certain)
olefinically unsaturated organo-titanates and organo-zirconates,

EXPRESS MAIL CERTIFICATE

Date 2/26/90 Label No US 410 326 642
I hereby certify that, on the date indicated above I
deposited this paper or fee with the U.S. Postal Service
& that it was addressed for delivery to the Commissioner
of Patents & Trademarks, Washington, DC 20231 by "Express
Mail Post Office to Addressee" service.

Ronald R. Rabin Ronald R. Rabin
Name (Print) Signature

when added to the manufacturing recipes of various addition
polymers (e.g., polyethylene, polystyrene, polyvinyl chloride,
polyvinylidene chloride and ethylene vinylacetate) and certain
condensation polymers (e.g., polycaprolactam, "nylon 6" and
5 polyethylene terephthalate "polyester") produce polymers which
have superior processibility and physical properties while having
substantially reduced persistence under landfill conditions.

The proportions of the additive(s) required to achieve
the persistence reduction varies greatly from system to system,
10 but generally useful results may be achieved by additions of from
0.01 to about 10% by weight of polymer.

The ability of the organo-metallic compounds to degrade
the polymers is enhanced by the presence of a combination of
saline water and a small proportion of alkali such as alkali and
15 alkaline earth hydroxides and carbonates. The combination of
alkali and aqueous salinity reduces the level of the organo-
titanium or organo-zirconium pyrophosphates to or even below
0.001 wt. % of polymeric wastes treated. Furthermore, the
presence of such materials makes it feasible to use organo-
20 metallics which, while alkali-soluble, are sufficiently water-
soluble to provide practicable benefits under neutral or acidic
conditions.

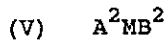
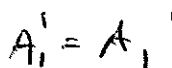
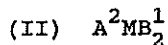
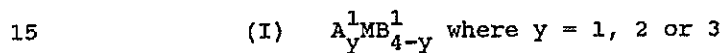
While not fully understood, it may be postulated that the
degradation of thermoplastics is enhanced by the additives of the
25 instant invention due to a combination of catalytic, hydrolytic,
oxidative and repolymerization phenomena.

Detailed Description of the Invention

The subject invention may be applied to a broad range of thermoplastic materials. These include polyolefins such as polyethylene and polypropylene, copolymers thereof including
5 ethylene, propylene copolymers and ethylene-styrene copolymers, polystyrenes and polyesters such as polyethylene terephthalate and polybutylene terephthalate.

The organo-titanium and organo-zirconium pyrophosphates of the invention are preferably substituted with one or more
10 allyl, alkenyl, acryl or methacryl groups or mixtures thereof. These compounds may be represented by the following general formulas:

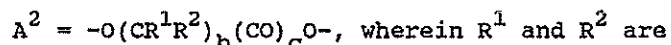
Table I



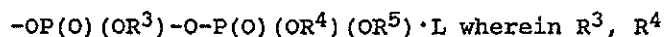
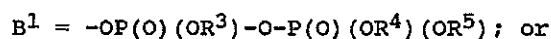
where M = Ti or Zr;

$A^1 = (RO)_a$, wherein R is an alkyl, alkenyl, or

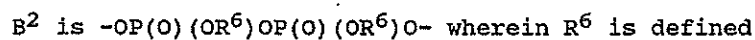
aralkyl group having less than 20 carbon atoms;



5 independently selected from hydrogen, alkyl, alkenyl, aralkyl and unsubstituted or ether-substituted aryl or alkaryl having less than 20 carbon atoms, b is 1 or 2 and c is 0 or 1;



10 and R^5 are each independently selected from hydrogen, alkyl having from 1 to 20 carbons, alkenyl having from 3 to 20 carbons, aralkyl and alkaryl having from 7 to 20 carbon atoms, each of said groups may be substituted by up to 3 ether oxygens, aryl having from 6 to 20 carbons and substituted aryl groups having up
15 to 5 halogens per aromatic ring; providing, however, that one and only one of R^3 , R^4 and R^5 is hydrogen; and each L is independently selected from tertiary monoamines containing alkali metals and alkaline earth metals.



20 as R^3 , R^4 , R^5 above except R^6 cannot be hydrogen.

Particularly preferred compounds of the present invention are set forth in the following table:

TNR = 10 pt font

Table II

<u>Code</u>	<u>Compound</u>	<u>Structural Formula</u>
A	Titanium IV (bis 2,2-propenolatomethyl) butanolato, tris (bis octyl) diphosphato-O, adduct with 2 moles of N,N-dimethylamino propyl (2-methyl) propenamide	ATiB ₃ ·3J
B	Titanium IV bis(bis octyl) diphosphato-O, ethanediolato, adduct with 2 moles of N,N-dimethylaminoethyl (2-methyl) propenoate	[OC ₂ H ₄ O]TiB ₂ ·2(CH ₃) ₂ NC ₂ H ₄ - OC(O)C(CH ₃)=CH ₂
C	Titanium IV bis(bis octyl) diphosphato-O, ethanediolato, adduct with 2 moles of N,N-dimethylaminoethanolato ethanol	[OC ₂ H ₄ O]TiB ₂ ·2(CH ₃) ₂ NC ₂ H ₄ - OC ₂ H ₄ OH
D	Titanium IV bis(bis octyl) diphosphato-O, ethanediolato, adduct with 2 moles of (bis octyl) phosphite	[OC ₂ H ₄ O]TiB ₂ ·HP(O)(OC ₁₃ H ₂₇) ₂

E	Zirconium IV bis(bis octyl) diphosphato-O, (bis-2,2 methyl- 1,3-propanediolato, adduct with 2 moles of N,N-dimethylamino propyl (2-methyl) propenamide	$EZrB_2 \cdot 2J$
5		
F	Zirconium IV bis(bis octyl) diphosphato-O, (bis 2,2- methyl)-1,3-propanediolato, adduct with 2 moles of triethanolamine	$EZrB_2 \cdot 2N(C_2H_4OH)_3$
10		
G	Titanium IV bis(bis methyl) diphosphato-O, ethanediolato, adduct with 2 moles of 2-N,N- dimethylamino (2-methyl) propanol	$[OC_2H_4O]Ti[OP(O)(OF)OP(O)-$ $(OF^1)(OF^2)]_2 \cdot 2D$
15		
H	Titanium IV bis(bis methyl) diphosphato-O, oxoethanediolato adduct with 2 moles of 2-N,N- dimethylamino (2-methyl) propenol	$[OCH_2C(O)O]Ti[OP(O)(OF)OP-$ $(O)(OF^1)(OF^2)]_2 \cdot 2D$
20		

5	<p>J Titanium IV bis(bis 2,2-propenolatomethyl) butanolato, bis(methylbutyl) diphosphato-O, adduct with 3 moles of N,N-dimethylaminopropyl(2-methyl) propanamide</p>	$\text{ATi}[\text{OP}(\text{O})(\text{OG})\text{OP}(\text{OG}^1)(\text{OG}^2)]_3 \cdot 3\text{J}$
10	<p>K Titanium IV (bis 2,2-methyl) propanolato, tris(bis octyl) diphosphato-O, adduct with 3 moles of N(vinyl)pyrrolidone</p>	$(\text{CH}_3)_3\text{CCH}_2\text{OTiB}_3 \cdot 3(\text{CH}_2=\text{CH})\text{NC}_4\text{H}_4$
15	<p>L Titanium IV bis(bis octyl) diphosphato-O, oxoethanediolato, adduct with 2 moles of N,N-dimethylamino (2-methyl) propanol</p>	$[\text{OCH}_2\text{C}(\text{O})\text{O}]\text{TiB}_2 \cdot 2\text{D}$
20	<p>M Zirconium IV bis (ethyl, 2-propyl) diphosphato-O, (bis 2,2-methyl) propanediolato, adduct with 2 moles of N,N-dimethylamino (2-methyl) propanol</p>	$\text{EZr}[\text{OP}(\text{O})(\text{OK})\text{OP}(\text{O})(\text{OK}^1)(\text{OK}^2)]_2 \cdot 2\text{D}$

<p>N 5</p>	<p>Zirconium IV bis (bis ethanolatopropyl) diphosphato-O, (bis 2,2-methyl propanediolato, adduct with 2 moles of N,N-dimethylamino propyl (2-methyl) propenamide</p>	$\text{EZr}[\text{OP}(\text{O})(\text{OL})\text{OP}(\text{O})(\text{OL}^1)-(\text{OL}^2)] \cdot 2\text{J}$
<p>10</p>	<p>Zirconium IV bis (bis methyl) diphosphato-O, propanediolato, adduct with 2 moles of N,N-dimethylaminopropyl (2-methyl) propenamide</p>	$[\text{OC}_3\text{H}_6\text{O}]\text{Zr}[\text{OP}(\text{O})(\text{OF})\text{OP}(\text{O})(\text{OF}^1)(\text{OF}^2)]_2 \cdot 2\text{J}$

wherein A = $(\text{CH}_2=\text{CHCH}_2\text{OCH}_2)_2(\text{C}_2\text{H}_5)\text{CCH}_2\text{O}$

B = $\text{OP}(\text{O})(\text{OX})\text{OP}(\text{OX}^1)(\text{OX}^2)(\text{O})$, two of $\text{X}^1, \text{X}^2, \text{X} =$

$\text{CH}_2\text{C}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$ and one of $\text{X}, \text{X}^1, \text{X}^2 = \text{H}$

15 D = $(\text{CH}_3)_2\text{NC}(\text{CH}_3)_2\text{CH}_2\text{OH}$

E = $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{O})_2$

F, F^1, F^2 : one of $\text{F}, \text{F}^1, \text{F}^2 = \text{H}$, and two = CH_3

G, G^1, G^2 : one of $\text{G}, \text{G}^1, \text{G}^2 = \text{H}$, one = CH_3 , and one = C_6H_5

J = $(\text{CH}_3)_2\text{NC}_3\text{H}_6\text{NC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$

20 K, K^1, K^2 : one of $\text{K}, \text{K}^1, \text{K}^2 = \text{H}$, one = C_2H_5 , and one =

$\text{C}(\text{CH}_3)_2$

L, L^1, L^2 : one of $\text{L}, \text{L}^1, \text{L}^2 = \text{H}$, and two = $\text{C}_2\text{H}_5\text{OC}_3\text{H}_6$

Generally speaking, from 0.001 to 10 wt. % of the organo-metallic compounds are added, preferably from 0.01 to 5 wt. %, based on the weight of the polymer. The polymer may also contain other additives, such as pigments, fillers, reinforcing agents, 5 comprising up to about 70% of the total thermoplastic composition and minor amounts of lubricants, stabilizers, processing aids and/or impact modifiers.

As noted previously, the environmental degradation of the thermoplastic materials heretofore noted may be enhanced by 10 exposing the polymers or articles fabricated therefrom to a saline solution containing 1 to 10% of the organo-metallic compounds. By "saline solution" is meant a solution containing from about 1 to 6 wt. % of salt. The salt used to form the saline solution is generally ordinary sodium chloride, though 15 other materials such as potassium chloride or calcium nitrate may be used.

Optionally, the solution should also contain from 1 to 20 wt. % of an alkali or alkaline earth metal hydroxide or carbonate. The most preferred alkaline materials are sodium, 20 potassium and calcium hydroxides and carbonates. The alkaline material should be present in an amount of from 1 to 20% by weight of the polymer. The degradation process takes place most effectively at a temperature in the range of from 80° to 200°F.

The organo-metallic pyrophosphates of the invention may 25 be prepared in accordance with the teaching of U.S. Patent Nos.

4,027,402; 4,122,062; 4,277,415; and 4,634,785, the disclosures of which are incorporated by reference herein.

In addition to the foregoing constituents, it has been found that packing the plastic to be decomposed in soil hastens the decomposition process. While it is not exactly understood why soil accelerates the decomposition, it is believed that the process is accelerated by the presence of humus in the soil.

The following examples are set forth to further elucidate the instant invention:

10 Example 1

This example shows the use of water-soluble organic titanates and zirconates to enhance the degradation of thermoplastics in preexistent landfills.

A controlled portion of a conventional stratified landfill (waste earth fill layers) containing implanted sheets of polyethylene and polystyrene at various levels is flooded with a solution of 5.6 wt. % of each of the organo-metallic titanate or zirconate set forth in Table II and 5% salt water and permitted to stand at an ambient temperature ranging from about 45°F to about 80°F. A control section adjacent thereto was also flooded with 5% salt water. When exhumed after thirty days, each of the test specimens shows substantial degradation in the form of crazing and perforations, whereas the control specimens show no visible signs of modification.

Example 2

This example shows the use of certain organo-metallic titanates and zirconates to enhance the environmental degradation of polyolefins and polystyrene. Polyethylene, polypropylene, polystyrene and polyester (polyethylene terephthalate) sheets are prepared by individually compounding 2 wt. % of organo-metallic titanates (A,C,G of Table II) and zirconates (E,F,M of Table I) into appropriate commercial resin base stocks. Control specimens without additives are also proposed.

The sheets are buried in a conventional landfill and permitted to remain undisturbed for three months. Visual evaluation of unearthed samples shows that the additive-containing specimens have undergone significantly more degradation than the control specimens.

Example 3

In this example, certain organo-titanates and organo-zirconates are employed as co-monomers in the manufacture of polyolefin (polyethylene), polystyrene and thermoplastic (ethylene-propylene) elastomer polymers.

Conventional processes and recipes are employed, except that in test specimens 0.08 wt. % of organo-metallic titanates J, K and L of Table II and organo-zirconates O, N and P of Table II are added uniformly to each monomer. The resulting polymers and controls containing no additive are processed and tested as described in Example 2, but without the addition of further

organo-metallic compounds. In each instance the test specimen containing the additives of the instant invention is found to have undergone substantially greater environmentally-generated degradation than the corresponding control.

5 Example 4

This example shows the use of a combination of organo-titanate and organo-zirconate pyrophosphates in the presence of alkaline aqueous saline to enhance degradation of organic polymers under landfill conditions.

10 Thin sheets or other fabricated entities are coated with aqueous solutions having from about 2 to 10 wt. % salt, from about 1 to 10 wt. % of an alkali and/or alkaline earth hydroxide, oxide and/or carbonate, and from about 1000 ppm to about 10 wt. % collectively of one or more of the indicated organo-metallic
15 pyrophosphates in Table No. II. From 0.5 to about 20 wt. % of coating per unit polymer is used. The coated materials are interred in a conventional post-consumer waste landfill, e.g., a municipal sanitary landfill, for a period of between thirty days and six months. The exhumed test specimens of polyolefins,
20 styrenics, and nylon polymers are found to have undergone significant degradation as evidenced by crazing, cracks, partial dissolution and/or severe mechanical degradation. On the other hand, except for the thermoplastic polyester and nylon specimens exposed to high levels of caustic, the untreated specimens show
25 negligible environmental degradation. While the thermoplastic

polyester and nylon samples exposed to caustic/carbonate environments containing more than about 1 wt. % alkali show significant degradation as compared to non-caustic-containing controls, even these materials show synergistic degradation in the presence of organic titanium and/or zirconium pyrophosphates.

Example 5

To further demonstrate the efficacy of the instant invention, a series of six tests were performed to show the effect of the process of the instant invention with ethylene vinyl acetate (EVA), polystyrene (PS) and linear low density polyethylene (LLDPE). In each of the tests where the substrate was treated with salt, the salt solution was present at a concentration of 5%. The organo-titanate added was LICA 38J at a concentration of 5.6% based on the resin when added internally to the substrate at the time of compounding. In the runs where the organo-titanate was added to the treating solution, 5.6% was added based on the weight of the solution. To show the effect of alkali, lime and KOH were added to certain of the aqueous treating solutions. The condition of the treated film was reported based on the following scale:

- 1 - Film substantially unaffected
- 2 - Film showed noticeable crazing and/or discoloration
- 3 - Film showed noticeable crazing and perforation through at least some of the surface

4 - Substantial deterioration of the film (loss of dimensional integrity)

Test I

In this test, sheets of EVA, PS and LLDPE were placed in a bucket in an oven at a temperature of 100°C for 40 days. In accordance with the invention, each of the substrates contained the aforementioned organo-titanate. Controls without titanates were likewise subjected to this accelerated aging test. Inspection showed test specimens with the titanate for EVA and PS were rated at 4 and with LLDPE rated 3. Without the titanate, all specimens rated 1.

Test II

In this biodegradability test, LLDPE, EVA and PS were treated under three separate sets of conditions. In each case, the substrate was packed in soil in a 2-gal. pail and maintained at ambient temperature. The control used was the EVA sheet packed in soil and treated with 0.04 wt. % of a 5% saline solution. In the first run, the EVA was compounded with 5.6 parts of the organo-titanate. In the second run, the organo-titanate containing EVA was packed in the soil in the presence of water; no salt was present. In the third run, the EVA was free of any internal organo-titanate and the treating solution was saline containing 5.6% of the organo-titanate.

After 15 days, the sheets were unearthed from the buckets and inspected. The following results were obtained:

Table A

	<u>Run</u>	<u>Substrate</u>	<u>Organo-Titanate</u>	<u>Salt</u>	<u>Condition</u>
5	Control	LLDPE	None	Yes	1
	A	LLDPE	Internal	Yes	3
	B	LLDPE	External	Yes	1
	C	LLDPE	Internal	No	1
	Control	EVA	None	Yes	2
10	A	EVA	Internal	Yes	4
	B	EVA	External	Yes	2
	C	EVA	Internal	No	4
	Control	PS	None	Yes	1
	A	PS	Internal	Yes	4
15	B	PS	External	Yes	2
	C	PS	Internal	No	3+

Test IV

In this test, PS substrates were placed in a 2-gal. pail packed in soil. Each set of runs compares the effect of the treatment on the PS substrate with and without the organo-titanates at temperatures of 25°C and 100°C. In each case, the treating solution contained salt.

Table B

<u>Organo-Titanate</u>	<u>Temperature</u>	<u>Condition</u>
Internal	100°C	4
None	100°C	3
5 Internal	20°C	3
None	20°C	1

In each of the above experiments, the substrates were inspected after 30 days. Where the temperature is indicated as 100°C, the bucket containing the substrate was cooked in an oven.

10 The above table clearly shows that the presence of the titanate accelerates the deterioration of the substrate.