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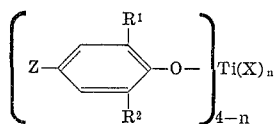
## PHENYL TITANIUM ESTERS AND PREPARATIONS THEREOF

Alvin F. Shepard and Bobby F. Dannels, Grand Island, N.Y., assignors to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York  
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This invention relates to novel esters of titanium. More particularly, it relates to esters of titanium that are hydrolytically stable, a process for making them, and uses of the esters.

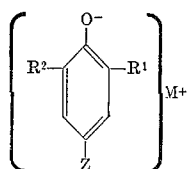
Triphenoxy and substituted triphenoxy titanium halide compounds have been prepared and are known in the art. These compounds, however, have a tendency to be hydrolyzed when exposed to moisture or other hydrolytic conditions. Under conditions of hydrolysis, the known compounds will hydrolyze to a phenol and an oxide or hydroxide of titanium.

In accordance with this invention it has been found that titanium esters having good resistance to hydrolysis are of the formula



wherein R<sup>1</sup> and R<sup>2</sup> are the same or different and are selected from the group consisting of alkyl having from 3 to about 20 carbons and aralkyl having from 7 to about 24 carbons, Z is selected from the group consisting of alkyl having from 1 to about 20 carbons, aralkyl having from 7 to about 24 carbons and halogen, X is a halogen and n is 0 to 1.

These esters of titanium may be prepared by reacting an alkali metal phenate having the formula



wherein R<sup>1</sup>, R<sup>2</sup>, and Z are as defined above and M is an alkali metal such as lithium, sodium, potassium, rubidium and cesium, with titanium tetrahalide in a molar ratio of at least about 3:1. Molar ratios of alkali metal phenate to the tetrahalide of up to 6 to 1 are also useful and give favorable results.

Examples of the alkali metal phenates that may be utilized in the practice of this invention are

sodium 2,6-di-tertiary-butyl-4-butylphenate,  
potassium 2,6-di-tertiary-amyl-4-chlorophenate,  
potassium 2,6-di(1,1,3,3-tetramethylbutyl)-4-benzylphenate,  
sodium 2-tertiary-butyl-6-tertiary-amyl-4-bromophenate,  
potassium 2,6-di(1,1,2,2-tetramethylpropyl)-4-phenylethylphenate,  
sodium 2,6-di(1-methyl-1-ethylamyl)-4-didodecylphenate,  
sodium 2,6-diisopropyl-4-methylphenate,  
sodium (2,4,6-triphenethyl)phenate,  
potassium 2,6-di-tertiary-butyl-4-nonylphenate,  
potassium 2,4,6-tri-tertiary-butylphenate,  
sodium 2,6-didodecyl-4-bromophenate,  
potassium 2,6-di-tertiary-butyl-4-chlorophenate,  
potassium 2,6-di-tertiary-butyl-4-bromophenate,  
sodium 2,6-di-tertiary-butyl-4-methylphenate,  
potassium 2,6-dinonyl-4-hexylphenate, and so forth.

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Examples of titanium tetrahalides that may be utilized are titanium tetrachloride, titanium tetrabromide, titanium tetrafluoride, and titanium tetraiodide, the preferred titanium compound being titanium tetrachloride. From the standpoint of favorable economics, and useful reactivity, sodium phenate salts of the above described phenates are the most advantageous and are particularly preferred.

The reaction of titanium tetrahalide and the alkali metal phenate is carried out at a temperature of from about 5 to about 250 degrees centigrade, it being preferable to maintain the temperature level at from about 100 to 150 degrees centigrade. The tetra ester of the titanium is formed by utilizing a higher temperature of this range, e.g., from about 150 to 250 degrees centigrade. Subatmospheric and superatmospheric pressures may be utilized, in addition to the more common atmospheric pressure. Also, the reactants can be added to one another, and mixed in any convenient manner.

The titanium esters of this invention have been found to improve the lubricating quality of petroleum oils. Between 0.001 and 5 percent of the titanium compounds of this invention may be utilized, with surprisingly good results being obtained when using from 0.5 to 2 percent of the instant compounds in the oil, on a weight basis. Examples of oils are: Sun 96, a straight Gulf Coast oil, having a Saybolt Universal viscosity of 2,000 seconds at 100 degrees Fahrenheit and 87 seconds at 210 degrees Fahrenheit; Standard of Indiana Gear Oil (Mid-Continent), having a Saybolt Universal viscosity of 1,500 seconds at 100 degrees Fahrenheit and 100 seconds at 110 degrees Fahrenheit; Society of Automotive Engineers Classification, 60 Motor Oil, having a Saybolt Universal viscosity of about 1,300 seconds at 110 degrees Fahrenheit; Cities Service "600-F1," manufactured by Cities Service, New York, N.Y.; Ashland "301-SR"; and Gulf Paratox, having a Saybolt Universal viscosity of about 1,200 seconds at 100 degrees Fahrenheit; such oils are improved by the present esters. The invented compounds may also be utilized as catalysts in the polymerization of olefins, for example, in the preparation of polypropylene. Examples of products of this invention are

tris(2,6-di-tertiary-butyl-4-butylphenyl)chlorotitanate,  
tetra(2,6-di-tertiary-butyl-4-butylphenyl)titanate,  
tris(2,6-di-tertiary-amyl-4-chlorophenyl)bromotitanate,  
tetra(2,6-di-tertiary-amyl-4-chlorophenyl)titanate,  
tris[2,6-(1,1,3,3-tetra-methylbutyl)-4-benzylphenyl]iodotitanate,  
tetra[2,6-(1,1,3,3-tetramethylbutyl)-4-benzylphenyl]titanate,  
tris(2-tertiary-butyl-6-tertiary-amyl-4-bromophenyl)chlorotitanate,  
tetra(2-tertiary-butyl-6-tertiary-amyl-4-bromophenyl)titanate,  
tris[2,6-di(1,1,2,2-tetramethylpropyl)-4-phenylethylphenyl]chlorotitanate,  
tetra[2,6-di(1,1,2,2-tetramethylpropyl)-4-phenylethylphenyl]titanate,  
tris[2,6-di(1-methyl-1-ethylamyl)-4-dodecylphenyl]chlorotitanate,  
tetra[2,6-di(1-methyl-1-ethylamyl)-4-dodecylphenyl]iodotitanate, and so forth.

The following examples illustrate the invention, but are not to be interpreted as limiting it in any respect. All parts are by weight and temperatures are in degrees centigrade, unless otherwise stated.

### EXAMPLE 1

Tris(2,4,6-tri-tertiary-butyl)chlorotitanate

Sodium 2,4,6-tri-tertiary-butylphenate was prepared by reacting 2,4,6-tri-tertiary-butylphenol (131 parts) dis-

solved in toluene (800 parts) with sodium methylate (27 parts). This mixture was refluxed at a temperature of about 115 degrees centigrade for a period of about 16 hours. The reaction mixture was distilled with some reflux at a temperature of from about 96 degrees centigrade to about 110 degrees centigrade. The distillation was continued until the distillate was free of methanol. The sodium salt of the phenate in toluene was cooled to about 28 degrees centigrade. Titanium tetrachloride (23.6 parts) was then added to the reaction mixture. The exothermic

This compound was refluxed with water for 6 days and hydrolyzed only 22 percent, as indicated by tests for chlorine evolution. It showed similar results in acid and alkaline mediums. The product was refluxed in 0.05 Normal sodium hydroxide for 6 days with a recovery, during this period of only about 30 percent of the theoretical amount of phenol.

In the following examples when the alkali metal phenate is reacted with the titanium tetrahalide, the product illustrated is formed.

Example No.	Alkali Metal phenate	Titanium tetrahalide	Product
3.....	Sodium 2,6-di-tertiary-butyl-4-butyl phenate.	Titanium tetrachloride.	Tris(2,6-di-tertiary-butyl-4-butyl-phenyl)chlorotitanate.
4.....	Potassium 2,6-di-tertiary-amyl-4-chlorophenate.	Titanium tetraiodide.	Tris(2,6-di-tertiary-amyl-4-chlorophenyl)iodotitanate.
5.....	Sodium (2,4,6-tri-phenylethyl)phenate	Titanium tetrabromide.	Tris(2,4,6-triphenethyl-phenyl) bromotitanate.
6.....	Sodium 2,6-didodecyl-4-bromophenate.	Titanium tetrachloride.	Tris(2,6-didodecyl-4-bromophenyl) chlorotitanate.

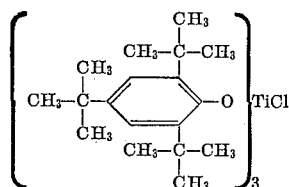
reaction which occurred was maintained at a temperature of about 45 degrees centigrade. This mixture was then refluxed for a period of about 48 hours at a temperature of from 105 to 120 degrees centigrade. The reaction mixture was cooled to room temperature and was poured into a water bath held at a temperature of from 5 to 20 degrees centigrade. The resulting solids were then purified by dissolving in hexane. Reddish-brown crystals of tris(2,4,6 - tri-tertiary-butyl)chlorotitanate were formed which had a melting point of 294-296 degrees centigrade.

#### EXAMPLE 2

##### Tris(2,4,6-tri-tertiary-butyl)chlorotitanate

The sodium salt of 2,4,6-tri-tertiary-butylphenol was prepared by dissolving 2,4,6-tri-tertiary-butylphenol (131 parts) in diethylene glycol dimethyl ether (190 parts) at 100 degrees centigrade. Sodium (11.5 parts), cut in small pieces, was slowly added to the above mixture. Heating was continued until the sodium was completely dissolved in the reaction mixture. The sodium phenate thus formed was completely soluble in the hot solvent. Titanium tetrachloride (13.8 parts) was added to this reaction mixture at about 100 degrees centigrade at a rate of 0.1 part to 0.2 part per minute. The resulting mixture was then heated at a temperature of from about 100 degrees centigrade to about 110 degrees centigrade for a period of about 21 hours. The reaction mixture was allowed to cool to room temperature and was poured into an ice bath. Solids formed as a result of this procedure were then dissolved in hexane (2000 parts). A solid residue was recovered which amounted to 6.6 parts. The hexane solvent was evaporated and the resulting solid was washed with 2000 parts of acetone at about 50 degrees centigrade. The crystalline residue was then recrystallized from hexane. The melting point of the resulting product was 294-295 degrees centigrade.

Analysis of the product, tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate having the structure



was as follows:

	Calculated	Found
Percent carbon.....	74.8	75.04
Percent hydrogen.....	10.1	10.19
Percent chlorine.....	3.6	4.08
Percent titanium.....	5.52	5.45
Molecular weight.....	868	854

It is to be understood that the triesters are prepared at temperatures in the range of from about 95 to about 180 degrees centigrade. The corresponding tetraesters may be formed by applying higher temperature conditions, e.g., from about 185 to 250 degrees centigrade.

#### EXAMPLE 7

2,4,6-tri-tertiary-butylphenyl chlorotitanate (1.5 percent by weight) was added to Sun 96-Oil and the resulting oil was tested in a Falex oil testing machine. This machine measures the torque (inch-pounds) resulting when grooved steel blocks are pressed against a rotating pin while bathed in the oil being tested. The angle of contact between the block and pin is such that the possibility of building up a hydrodynamic film of oil is negligible, thus depending entirely on the deposition of a protective film by chemical action or by adsorption to prevent metal-to-metal contact and seizure. An initial run at a light load is made in order to give the oil a chance to initiate this film-building action, and then the load is progressively increased by means of a ratchet which acts on a toothed wheel to tighten the jaws. The results of this test showed that the titanate compound of the invention had lubricating power.

Similar results are obtained when tris(2,6 - di - tertiary-butyl - 4 - butylphenyl)chlorotitanate, tris(2,6-di-tertiary-amyl - 4 - chlorophenyl)iodotitanate, tris(2,4,6-triphenylethylphenyl)bromotitanate and 2,6 - (didodecyl - 4 - bromophenyl)chlorotitanate are added to Cities Service "600-F1," Ashland "301-SR" and Gulf Paratax.

The additives of this invention also find important utility as antioxidants in a wide variety of oxygen sensitive materials; thus, liquid and solid products derived from crude petroleum will be found to possess increased storage stability by the use of the antioxidant of this invention. For example, gasoline, jet fuel, kerosene, fuel oil, turbine oils, insulating oils, motor oils and various waxes have increased oxidative stability when they contain an antioxidant of this invention. Likewise, liquid hydrocarbon fuels which contain organometallic additives such as tetraethyllead, and other organometallic compositions which are used as fuel additives attain appreciably increased oxidative stability by the practice of this invention. Furthermore, such fuels which contain halogen and phosphorus-containing scavengers for these organometallic compounds are benefited by the practice of this invention. In addition to increased storage stability, lubricating oils and functional fluids, such as automatic transmission and hydraulic fluids, both those derived from naturally occurring hydrocarbons and those synthetically prepared, will achieve a high degree of resistance to oxidation during use at elevated temperatures by the practice of this invention. Lubricating oils may be employed at extremely high temperatures without undergoing oxidative degradation, when protected by an antioxidant of this invention. The addi-

tion of small quantities of the compositions of this invention to such materials as hydraulic, transformer and other highly refined industrial oils, as well as crankcase lubricating oils and lubricating greases prepared from these oils by the addition of metallic soaps, will greatly increase their resistance to deterioration in the presence of air, oxygen or ozone. Furthermore, the organic soaps used in the preparation of lubricating greases will become stabilized by the practice of this invention.

Organometallic compositions such as tetraethyl lead and tetraethyl lead antiknock fluids containing halo-hydrocarbon scavengers as dyes and which may contain various phosphorus compounds and other organometallic additives, will be stabilized against deterioration during storage by the addition thereto of an antioxidant quantity of a compound, or mixture of compounds, of the invention.

The hydrolytically stable compounds of this invention are also extremely effective antioxidants for elastomers, including high molecular weight unsaturated hydrocarbon polymers, both derived from naturally occurring sources and those synthetically prepared. Thus, natural rubbers and synthetic rubbers, including oil extended rubbers and sulfur vulcanized rubbers will be greatly benefited by the practice of this invention. Examples of the synthetic rubbers protected by the practice of this invention include such synthetics as polybutadiene, methyl rubber, polybutadiene rubber, butyl rubber, GR-S rubber, GR-N rubber, piperylene rubber and dimethylbutadiene rubber.

The practice of this invention is also useful in protecting paraffin and microcrystalline petroleum waxes against the oxidative deterioration which leads to rancidity. Furthermore, the compounds of this invention are extremely useful in the stabilization of fats and oils of animal or vegetable origin, which become rancid during periods of storage due to oxidative deterioration. Typical animal fats benefited by the practice of this invention include butterfat, lard, beef tallow, fish oils, such as cod liver oil, as well as various foods containing or prepared in animal fats which tend to deteriorate. These include, for example, potato chips, fried fish, donuts, crackers, and various types of pastry, such as cakes and cookies. Furthermore, fat fortified animal feeds and fish meals used as animal feeds are greatly benefited by the practice of this invention. Not only are these compositions protected against oxidative deterioration but the inclusion of a composition of this invention in such materials inhibits the degradation of vitamins A, D and E and certain of the B complex vitamins. Examples of compositions containing oils derived from vegetable sources which are benefited by the practice of this invention include castor oil, soybean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, citrus oils, cottonseed oil and various compositions containing these, including peanut butter, peanuts and other whole nuts, salad dressings, margarine and other vegetable shortenings.

The compounds of this invention are also antioxidants for various organic compounds and polymeric materials, including polystyrene, polyvinyl chloride, polyvinyl chloride containing an alkaline earth metal soap, such as barium laurate, polyvinyl acetate, various epoxide resins and polyester, resins and polymers including the alkyds. However, in particular the compounds of this invention are antioxidants for saturated hydrocarbon synthetic polymers derived from polymerization of an aliphatic monolefinic hydrocarbon compound having preferably up to 5 carbon atoms and only a single unit of unsaturation per monomeric molecule. Examples of such monomers include ethylene, propylene, butylene, isobutylene, 2-methyl-4-butene, 2-methyl-3-butene and the like. Thus the polymers are homopolymers and copolymers of ethylene, propylene, butylene, isobutylene and the pentenes and are usually solid. Polyethylene and polypropylene are preferred polymers in the practice of this invention and they are derived from the polymerization of ethylene and propylene respectively.

A preferred embodiment of this invention involves providing a lubricating oil normally susceptible to oxidative deterioration containing, in amount sufficient to inhibit such deterioration, a small quantity of the above compound as an additive. It has been found in actual practice that small amounts of the compounds or mixtures thereof very effectively stabilize lubricant compositions, e.g., petroleum hydrocarbon oils and synthetic oils, against oxidative deterioration.

The hydrolytically stable additives of this invention effectively stabilize such lubricating and industrial oils as crankcase lubricating oils, transformer oils, turbine oils, transmission fluids, cutting oils, gear oils, industrial oils, mineral white oils, glass annealing oils, and, in general, engine and industrial oils which are derived from crude petroleum and are normally susceptible to deterioration in the presence of air, particularly at elevated temperatures and most particularly in the presence of iron oxide.

In the lubricating oil compositions of this invention effective use can be made of other additives which are known to the art, such as detergent-dispersants, pour point depressants, viscosity index improvers, antifoam agents, rust inhibitors, oiliness or film strength agents, dyes, and the like. Typical of the detergent additives that can be used in the compositions of this invention are metallic soaps of high molecular weight acids, such as aluminium naphthenates, calcium phenylstearates, calcium alkyl salicylates, alkaline earth metal petroleum sulfonates, alkaline earth metal alkyl phenol sulfides (barium amyl phenol sulfide, calcium octyl phenol disulfide, etc.), metal salts of wax-substituted phenol derivatives, and the like. Of the viscosity index improvers and pour point depressants, effective use can be made of polymers of the esters of methacrylic acids and higher fatty alcohols and the corresponding polymers of esters of acrylic acid and higher fatty alcohols. These and other additives which can be employed in the compositions of this invention will now be well known to those skilled in the art.

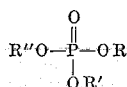
The synthetic lubricants which are enhanced by the practice of this invention are, in general, nonhydrocarbon organic compositions; i.e., organic compositions which contain elements other than carbon and hydrogen. Examples of general classes of material which are protected against oxidative deterioration by the practice of this invention include diester lubricants, silicones, halogen containing organic compounds, including the fluorocarbons; polyalkylene glycol lubricants, and organic phosphates which are suitable as hydraulic fluids and lubricants. The synthetic diester oils stabilized by the practice of this invention include sebacates, adipates, etc., which find particular use as aircraft instrument oils, hydraulic and damping fluids, and precision bearing lubricants. These diester oils are exceedingly difficult to stabilize under high temperature conditions. Use can be made of the diesters formed by the esterification of straight chain dibasic acids containing from 4 to about 16 carbon atoms with saturated aliphatic monohydric alcohols containing from 1 to about 10 carbon atoms. Of these diester oils, it is preferable that the alcohol used in their preparation be a branched chain alcohol because the resultant diesters have very valuable lubricating properties and the inhibitor of this invention very effectively stabilizes these materials against oxidative deterioration. Thus, use can be made of oxalates, malonates, succinates, glutarates, adipates, pimelates, suberates, azelates, sebacates, etc.

Another class of synthetic lubricants which achieve enhanced oxidative stability by the practice of this invention includes the "silicone" lubricants. The term "silicone" as used in the specification and claims of this application is defined as a synthetic compound containing silicon and organic groups.

The silicone oils and greases serving as the base medium for the lubricant compositions of the invention include the polysiloxane oils and greases of the type, polyalkyl-

polyaryl-, polyalkoxy-, and polyaryloxy-, such as polydimethyl-siloxane, polymethylphenyl siloxane, and polymethoxyphenoxy siloxane. Further included are silicate ester oils, such as tetraalkyloxy and tetraaryloxy silicates of the tetra-2-ethylhexyl and tetra-p-tert-butylphenyl types, and the silanes. Also included are the halogen substituted siloxanes, such as the chlorophenyl polysiloxanes.

Another important class of synthetic materials which are enhanced by the practice of this invention are phosphate esters which are, in general, prepared by the reaction of an organic alcohol with phosphoric acid and have the general formula:



where R, R' and R'' represent either hydrogen or an organic radical and where at least one of the groups represented by R, R' and R'' is an organic radical. Typical of these materials is tricresylphosphate. Other examples of phosphate esters include: tris(2-chloro-1-methylethyl) phosphate; tri-n-butyl-phosphate; tris(2-ethylhexyl) phosphate; triphenyl phosphate; tris(p-chlorophenyl) phosphate; diethyl-m-tolyl phosphate; p-chlorophenyl dimethyl phosphate; tris(2-n-butoxyethyl) phosphate; dimethyl-m-tolyl phosphate; di-n-propyl-m-tolyl phosphate; di-n-butyl-phenyl phosphate; 1,3-butylene-chloroisopropyl phosphate; methyl-d,m-tolyl phosphate; bis(2-chloro-1-methylethyl)-m-tolyl phosphate; dimethyl 3,5-xylyl phosphate; 4-chloro-m-tolyl dimethyl phosphate; 2-ethyl-1-n-propyl-trimethylene methyl phosphate; 4-chloro-m-tolyl-1-methyltrimethylene phosphate; dimethyl-n-octyl phosphate, and the like.

As noted above, the antioxidants of this invention are also excellent antioxidants for saturated hydrocarbon polymers, prepared from monoolefins having up to 5 carbon atoms. Polyethylene and polypropylene are, for example, hydrocarbon polymers derived from the polymerization of ethylene and propylene. Polymers of various types may advantageously be stabilized according to the present invention. The polymers which are employed may, for example, be similar to those which may be obtained by polymerizing ethylene in a basic aqueous medium and in the presence of polymerization having quantities of oxygen under relatively high pressure in excess of 500 or 1,000 atmospheres at temperatures between 150 and 275 degrees centigrade. Or, if desired, they may be similar to the essentially linear and unbranched polymers ordinarily having greater molecular weights which may be obtained under relatively low pressures of 1 to 100 atmospheres using such catalysts to polymerize the ethylene as mixtures of strong reducing agents and compounds of groups IV-B, V-B and VI-B metals of the periodic system; chromium oxide on silicated alumina; hexavalent molybdenum compounds; and charcoal supported nickel-cobalt. The polymer which results from these various polymerization processes may have a molecular weight in the range from 1300 to over 1,000,000, depending on the particular conditions of polymerization employed.

There are several methods available for preparing inhibited hydrocarbon polymer compositions. Thus the blending of the additives of this invention, with a polymer such as, for example, the polyethylene, may be carried out on open rolls, on internal mixers or may be accomplished by mixing with extrusion. It is also possible to prepare concentrated batches of the polymer containing excessive amounts of the additive and then mix the concentrate with additional polymer to prepare a composition of this invention. The preferred method of compounding the polymers is by milling on heated open rolls at slightly elevated temperatures by methods well known to the art. The temperature range employed is sometimes critical as certain polyethylenes will not melt at low temperatures and tend to stick to the rolls at high temperatures. The additive may be initially mixed with the polymer in the

dried state or may be first dissolved in a suitable solvent, then sprayed on the polymer and milled in.

In addition to the additives of this invention saturated hydrocarbon polymers may contain other compounding and coloring additives including minor proportions of carbon black, elastomers, polyvinyl compounds, carboxylic acid esters, urea-aldehyde condensation products, flame retarding agents such as antimony trioxide and chlorinated hydrocarbons and various pigment compositions designed to impart color to the finished product.

Other hydrocarbon polymers which are stabilized against oxidative deterioration according to this invention include natural rubber, GR-S and GR-N rubbers, butyl rubber, methyl rubber, polybutene rubber, butadiene rubbers, piperylene rubbers, dimethylbutadiene rubbers, polystyrene, polybutadiene, polyisobutylene, polyethylene, isobutylene-styrene copolymer and, in general elastomeric hydrocarbon polymers which are normally susceptible to oxidative deterioration. Such polymers are well known in the art and besides being susceptible of oxidative deterioration are characterized by having molecular weights above about 10,000.

The following examples illustrate various organic compositions described above.

#### EXAMPLE 8

To 100 parts of a thermolyzed tung oil was added 0.5 part of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate. This solution was applied to glass plates which were exposed to ultraviolet rays. After a period of three days the glass plates showed no signs of oxidation, whereas glass plates treated with thermolyzed tung oil only showed the effects of an oxidation.

#### EXAMPLE 9

At about 100 degrees centigrade, it was found that tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate substantially eliminated peroxidation of triisopropylbenzene.

#### EXAMPLE 10

To 100 parts of styrene was added 0.5 part of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate. This solution was exposed to the atmosphere for a period of about 20 hours. The viscosity of the solution did not change, indicating the ability of the additive to act as an antioxidant. Unmodified styrene turned viscous in a similar period of time.

#### EXAMPLE 11

The procedure of Example 10 was repeated but 0.5 part of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate was added to 100 parts of styrene. The resulting product was vastly improved over a control in its oxidative stability.

#### EXAMPLE 12

To 100 parts of freshly prepared aniline was added 0.5 part of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate. The oxidative stability of aniline subjected to air for a period of several days was greatly increased by the addition of this compound.

#### EXAMPLE 13

To 100 parts of freshly prepared aniline was added 0.05 part of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate. The oxidative stability of aniline was greatly increased by the addition of this compound. Utilizing tetra(2,4,6-tri-tertiary-butylphenyl)titanate gives similar results.

#### EXAMPLE 14

To 100 parts of a cis-polybutadiene rubber in excess benzene was added 0.5 percent of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate, based on the weight of the batch, and the solution was subjected to oxidizing conditions. After 96 hours this composition showed no signs of gelling. This indicates the antioxidation characteristic of this composition.

## EXAMPLE 15

Example 14 is repeated, utilizing 0.05 percent of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate based on the weight of the batch. Similar results are obtained.

## EXAMPLE 16

To natural rubber (Hevea), is added 0.1 percent of tris(2,6-di-tertiary-butyl-4-butylphenyl)chlorotitanate. This composition is improved in its oxidative stability.

## EXAMPLE 17

To 10,000 parts of a grade 115/145 aviation gasoline containing 4.5 milliliters of tetraethyl lead per gallon, which gasoline has an initial boiling point of 110 degrees Fahrenheit and a final boiling point of 330 degrees Fahrenheit, is added 0.5 percent of tetra(2,6-di-tertiary-butyl-4-butylphenyl)bromotitanate. This composition has improved antioxidation characteristics.

## EXAMPLE 18

With 100,000 parts of di(sec-amyl)sebacate having a viscosity at 210 degrees Fahrenheit of 33.8 Saybolt Universal seconds (SUS), a viscosity index of 133 and a molecular weight of 342.5, is blended 0.5 weight percent of tris(2,4,6-triphenethyl phenyl)bromotitanate. The resulting lubricant possesses greatly enhanced resistance against oxidative deterioration.

## EXAMPLE 19

To a siloxane fluid having a viscosity of 71 centistokes at 25 degrees centigrade and 24 centistokes at 75 degrees centigrade, a specific gravity of 1.03 at 25 degrees centigrade, a freezing point of -70 degrees centigrade and a flash point of 540 degrees Fahrenheit, which is composed of a halogen-substituted polyphenyl-polymethyl siloxane, is added sufficient tris(2,6-di-tertiary-amyl-4-chlorophenyl)iodotitanate to give a composition containing 1.5 percent of the additive. This oil composition is resistant to oxidative deterioration due to the presence of additive of this invention.

## EXAMPLE 20

To 1,000 parts of polyethylene produced by oxygen catalyzed reaction under a pressure of 20,000 atmospheres and having an average molecular weight of 40,000, are added and mixed 2 parts of tris(2,6-didodecyl-4-bromophenyl)chlorotitanate. The resulting composition has a greatly increased oxidative stability, over a control.

## EXAMPLE 21

To 1,000 parts of a solid isotactic polypropylene polymer having a density of 0.905 and a Rockwell hardness greater than 85, are added and blended 5 parts of tris(2,4,6-tri-tertiary-butylphenyl) bromotitanate. The composition formed has antioxidative qualities.

Titanium tetraesters such as tetra(tri-2,4,6-tertiary-butyl-phenyl)titanate, tetra(tri-2,6-tertiary-amyl-4-chlorophenyl)titanate, tetra(di-2,6-tertiary-butyl-4-decylphenyl)titanate and tetra(di-2,6-tertiary-butyl-4-bromophenyl)titanate, also give compositions that have antioxidant characteristics, when employed in similar proportions and in analogous materials in lieu of the triesters.

The additives of this invention are also extremely useful in inhibiting and stabilizing nonpetroleum fats and oils normally subject to the deteriorating effect of oxidative rancidity. In particular, compounds of this invention are excellent stabilizers for animal fats and oils, especially lard, against the effects of rancidity.

In formulating the stabilized nonpetroleum fats and oils of this invention, the additive or combination of additives is incorporated by appropriate means into the substrate to be stabilized. Thus, in the case of animal, vegetable and fish oils, the additive or combination of additives is added in appropriate quantity and the resulting mixture agitated to insure homogeneity. Where the substrate is a solid at room temperatures, e.g., fats, butter, etc., the mixing is

preferably carried out at temperatures above the melting point of the substrate. When a combination of additives is used, they can be mixed with the substrate as a preformed mixture or can be separately blended therewith in either order. Generally speaking, it is desirable to first dissolve the additive combination in high concentration in a small portion of the material to be stabilized. The resulting concentrated solution is then blended with the remaining bulk. Another way of facilitating the formulation of the composition of this invention is to predissolve the additive or combination of additives in a suitable solvent, such as ethanol, glycerol, propylene glycol, etc., and then mix the resultant solution with the material to be stabilized. However, the preferred way of formulating the compositions of this invention is to predissolve the additive mixture in a fatty acid partial ester of a polyhydroxy compound, notably a monoglyceride, and then blend this mixture with the material to be stabilized. The nature of these monoglyceride compositions is well known in the art and may be made from either animal or vegetable fats, with or without previous hydrogenation. These compositions generally contain about 40 percent of the mono-stearyl, monooleoyl, and/or monopalmityl glycerides or mixtures thereof with the balance comprising a mixture of di- and triglycerides. Molecularly distilled monoglycerides may also be used for this purpose. These compositions will be apparent from the following examples.

## EXAMPLE 22

With 1,000 parts of melted lard is mixed 1 part of tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate. After cooling, the lard can be stored for long periods of time without the development of rancidity.

## EXAMPLE 23

With 5,000 parts of cottonseed shortening are blended 5 parts of tris(2,6-di-tertiary-butyl-4-methylphenyl)bromotitanate. The resulting shortening has improved resistance against oxidative rancidity.

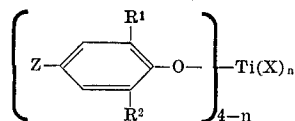
## EXAMPLE 24

To 10,000 parts of corn oil are added with stirring 20 parts of tris(2,6-di-tertiary-butyl-4-pentylphenyl)chlorotitanate. The resulting corn oil has improved storage stability characteristics.

While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention, as it is realized that substitutions therein are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, covering the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A titanium ester of the formula



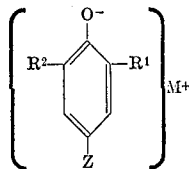
where R<sup>1</sup> and R<sup>2</sup> are selected from the group consisting of alkyl having from 3 to 19 carbons, and aralkyls having from 7 to about 24 carbons, Z is selected from the group consisting of alkyl having from 1 to about 20 carbons, aralkyl having from 7 to about 24 carbons and halogen, X is a halogen, and n is 0 to 1.

2. A titanium ester in accordance with claim 1 where- in R<sup>1</sup>, R<sup>2</sup> and Z are alkyl having from 3 to 19 carbons.

3. Tris(2,4,6-tri-tertiary-butylphenyl)chlorotitanate.

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4. A process for preparing a titanate ester comprising reacting in a molar ratio of at least about 3:1, an alkali metal phenate having the formula



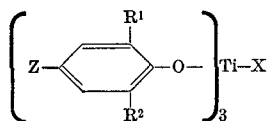
where R<sup>1</sup> and R<sup>2</sup> are selected from the group consisting of alkyl having from 3 to 20 carbons, and aralkyl having from 7 to about 24 carbons, and Z is selected from the group consisting of alkyl having from 1 to about 20 carbons, aralkyl having from 7 to about 24 carbons and halogen, and M is an alkali metal, with titanium tetrahalide.

5. A process in accordance with claim 4 wherein the alkali metal phenate is sodium 2,4,6-tri-tertiary-butylphenate.

6. A process in accordance with claim 4 wherein the titanium tetrahalide is titanium tetrachloride.

7. A process according to claim 4, in which said reacting takes place at a reaction temperature ranging from about 100 degrees centigrade to 250 degrees centigrade.

8. A titanium ester of the formula:



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where R<sup>1</sup> and R<sup>2</sup> are selected from the group consisting of alkyl having from 3 to 19 carbons, and aralkyls having from 7 to about 24 carbons, where Z is selected from the group consisting of alkyl having from 1 to about 20 carbons, aralkyl having from 7 to about 24 carbons and halogen, and where X is halogen.

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25 TOBIAS E. LEVOW, *Primary Examiner*.

H. M. S. SNEED, *Assistant Examiner*.

U.S. Cl. X.R.

30 252—431, 42.7, 400; 260—45.75

UNITED STATES PATENT OFFICE  
**CERTIFICATE OF CORRECTION**

Patent No. 3,418,348 Dated December 24, 1965

Inventor(s) Alvin F. Shepard and Bobby F. Dannels

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 73, the word after "percent" should read as---chlorine---.  
Column 4 in the Table under Product, next to the last line, the correct nomenclature should be---Tris(2,6-didodecyl-4-bromophenyl).---.  
Column 5, line 12, "as" should be corrected to read---or---.  
Column 7, line 17, the word after "either" should be corrected to read as---hydrogen---.

SIGNED AND  
SEALED  
MAY 26 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.  
Attesting Officer

WILLIAM E. SCHUYLER, JR.  
Commissioner of Patents