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2,960,469

LOAD CARRYING LUBRICANT

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20 Claims. (Cl. 252—42.7)

This invention relates to novel lubricating oil compositions. More specifically, my invention is concerned with lubricating oil compositions comprising a base oil of lubricating viscosity having incorporated therein certain organic compounds of titanium in an amount sufficient to impart increased load carrying capacity to the base oil. These titanium compounds find particular utility when incorporated in synthetic base oil lubricating compositions. In one particular aspect, I have found that the effectiveness of the titanium additives is materially enhanced by the provision of a small amount of free dibasic acid in the lubricant composition.

The demand for synthetic lubricants is ever increasing in view of, among other things, their low pour point, high viscosity index and low volatility for a given viscosity. The demand is particularly due to the present and coming widespread use of turbojet and turboprop engines for military and commercial aircraft. In these uses lubricants having mineral oil bases and containing additives to impart desired characteristics such as viscosity index improvement and extreme pressure properties, may not be satisfactory since these compositions are sources of deposits which can interfere with proper engine operation. Even though most synthetic lubricants have high viscosity indices, low volatilities and low pour points, the latter affording good low temperature starting characteristics, at least certain of these oils including those desired from the standpoint of stability and cost have insufficient load carrying capacity.

Specifications relating to synthetic lubricating oils have been promulgated or are being considered which set minimum load carrying capacity requirements. Gear loading in the turboprop engine is particularly high. Synthetic lubricants containing primarily carbon, hydrogen and oxygen are particularly desirable as they have many satisfactory characteristics and are not beyond a feasible price range. On the other hand, the load carrying capacity of these base oils is not sufficient to meet turbine engine specifications. It is then desirable to increase the load carrying capacity of these and other synthetic lubricant bases to adapt them for use in turbine engines and in other applications where extreme pressure properties are needed. The advantages of mineral oil lubricants having good load carrying capacity are widely known and the need for agents to provide this characteristic is apparent.

It has been proposed that the load carrying capacity of lubricants be increased by the addition of agents such as tricresyl phosphate and synthetic or natural thickeners. Tricresyl phosphate imparts extreme pressure properties but such are either insufficient or if sufficient other desirable properties of the base oil are frequently deleteriously affected by the phosphate addition. The use of thickeners, although meeting load carrying specifications, results in a fluid of high viscosity. This can be disadvantageous as some engine manufacturers wish a fluid having a low viscosity at reduced temperatures yet having the load carrying capacity of a more viscous lubricant.

In the present invention I have found that the load

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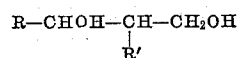
carrying capacity of lubricating oils can be substantially increased by incorporation of a minor amount of a titanium organic compound and the desired characteristics of the base oil are not deleteriously affected to a material extent. The titanium-containing organic materials can be used to impart extreme pressure characteristics to such oils provided for any given use, but most significantly my additives exhibit sufficient extreme pressure properties in synthetic oils, particularly those consisting essentially of carbon, hydrogen and oxygen, to satisfy specifications, including those of the military, now promulgated or being considered and of which I am aware. My additive compounds are further advantageous in that they need not thicken the lubricating oil regardless of the viscosity of the additive since only small amounts of my agents need be employed for most if not all uses.

The titanium-containing additives of my invention are compatible, i.e. soluble, dispersible or miscible, with the lubricating base oils and have the structure of those products obtained by reacting an organic titanium tetraester with a glycol. The additives might be derived from other reactant materials. The products can be titanium monomers or polymers, and, if desired, may be water-washed to approach a water-insensitive form. At least certain of the monomer and polymer additives are chelated and have a coordinate valence bond between an oxygen and a titanium atom. Generally, the mere addition of a titanium tetraester to a glycol initiates an exothermic reaction, although if desired heating can be employed. The reaction may proceed only to the monomer stage or continue to a polymer product directly. If a monomer or partially polymerized product is obtained, it may be further polymerized. In any event, I can employ the various products afforded which range from viscous liquids to solids and are compatible in the base oils.

I am aware that U.S. Patent No. 2,160,273, discloses that certain titanium tetraesters impart improved load carrying capacity to mineral oil based lubricants. However, such tetraesters have chemical structures different from those of the titanium-containing additives of the present invention. In fact, the titanium tetraesters are useful starting materials in the preparation of my additives. Moreover, the titanium tetraesters are unstable in the presence of water and can form titanium dioxide which is an oil-insoluble solid material not considered advisable for use in lubricating compositions.

Among the titanium esters which I can employ for reaction are alkyl titanates such as methyl, ethyl, propyl, butyl, 2-ethylhexyl, dodecyl, cyclohexyl and ethoxyethyl tetraesters; aryl tetraesters such as phenyl and betanaphthyl tetraestimates; aralkyl esters such as benzyl tetra-titanate; mixed esters such as diethyl diphenyl tetra-titanates; mixtures of these materials and their condensed or polymeric organic titanates. The various hydrocarbon esters can be substituted in the ester group although the unsubstituted esters are preferred. Those esters prepared from mono-functional alcohols are used most advantageously. Ordinarily the separate organic radicals of the titanium tetraester will contain up to about 12 or 18 carbon atoms but may contain more if desired.

Although the additive agents in my lubricant compositions are not limited thereto, the preferred agents are the products obtained through the reaction of the titanium tetraester with a glycol of the 1,3-diol type, see U.S. Patent No. 2,643,262, hereby incorporated by reference. As set forth in the patent these glycols are 2,3-diorgano hydrocarbon substituted materials which have the formula



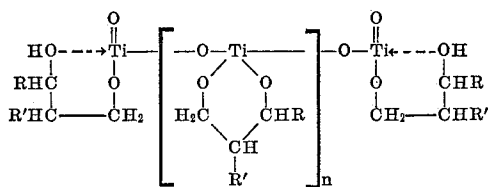
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The diorgano radicals, that is the R and R' of the glycol formula, can be alkyl, aryl or mixed, and if desired be substituted as with halogen, for instance chlorine. However, R and R' should be substantially non-reactive under the reaction and operating conditions employed. Generally, these glycols contain from about 5 to 12 carbon atoms, for instance an octylene glycol; however, if desired they could contain a greater number. Among the specific glycols which can be employed are 2-ethyl-1,3-hexane-diol, 2-propyl-1,3-heptanediol, 2-methyl-1,3-pentanediol, 2-butyl-1,3-butanediol, 2,4-diphenyl-1,3-butanediol, and 2,4-dimesityl-1,3-butanediol.

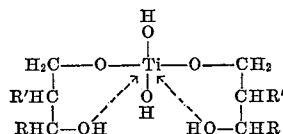
In addition to these glycols I can employ others and generally the glycols will contain from 2 to about 20 or 24 carbon atoms or more. Also, as indicated above, the glycols may be unsubstituted or substituted as with halogen or another hydroxy radical. Others of the glycols which I can use are ethylene glycol, 2,3-butanediol and ether polyalkylene glycols, for instance where the alkylene radical contains 2 to 4 carbon atoms such as diethylene glycol and dipropylene glycol.

I am not certain of the various structures of my titanium additive agents, but they can be in monomeric or polymeric form. Thus U.S. Patent No. 2,643,262 proposes the following structures for compounds resulting from combinations of various ratios of titanium tetraester and glycol.

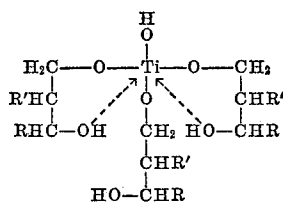
A. (1 molecule of Ti ester to 1 molecule of glycol.)



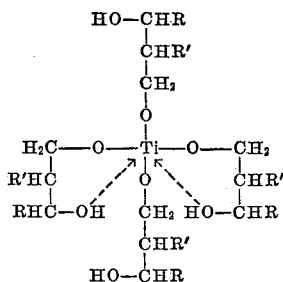
B. (1 molecule of Ti ester to 2 molecules of glycol.)



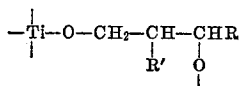
C. (1 molecule of Ti ester to 3 molecules of glycol.)



D. (1 molecule of Ti ester to 4 molecules of glycol.)

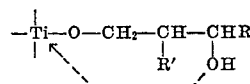


As noted in this patent, its various products are said to be characterized by having the structure

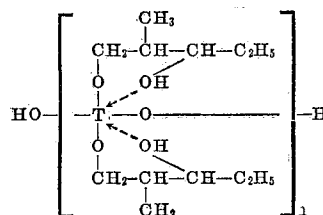


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or

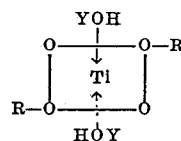


It is preferred to employ in the compositions of my invention the titanium ester-glycol reaction products which are relatively insensitive to water. In groups B and C above, the compositions shown are in this form, that is any ester group of the titanium tetraester remaining unreacted has been replaced by a hydroxy radical as through water-washing of the product. Also, the compounds of Group A above appear to be polymeric in form even though no extraneous heat is applied to the reaction as was the case in Example I of the said patent where the preparation of such a compound is described. In Example IV of this patent a polymer allegedly having the following formula was produced by heating in the presence of water the product from the reaction of 2 moles of 2-methyl-1,3-pentanediol and 1 mole of tetraisopropyl titanate.

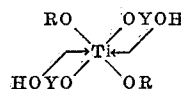


In this formula n is a number greater than 1. Also, from this patent it is apparent that the reaction of the glycol and the titanium ester can be conducted in the presence of inert solvents, e.g. cyclohexane, n-heptane, benzene, etc.

The preparation of the titanium compounds I employ as extreme pressure agents has also been considered in J.A.C.S., vol. 76, pages 2533-2536. The reaction is described as taking place between the titanium tetraester and a glycol to provide stable chelate compounds. It was postulated that when using 2 moles of glycol per mole of titanium ester the structure of the product would be

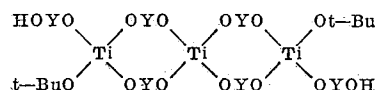


where R is the hydrocarbon radical of an original ester group and Y is the glycol hydrocarbon radical or residue, that is the glycol minus two essential hydroxy radicals. This structure might also be represented as



In either case, to produce a more water-insensitive material, the —OR groups could be replaced by hydroxy radicals through hydrolysis.

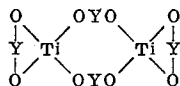
This J. A. C. S. publication concluded that manufacture of titanium ester-glycol reaction products having ester to glycol ratios of 1:1, 1:2 or 1:3 seems unlikely but possible combinations were 2:2, 2:3, 2:4 and 4:6. Thus, when reacting 2,3-butanediol with tetra tertiary-butyl titanate in the molar ratio of 2:1, the following polymeric structure was proposed.



The product from this reaction analyzed 17.5% titanium and corresponded to $\text{C}_{32}\text{H}_{68}\text{O}_{14}\text{Ti}_3$ (820.6 M.W.).

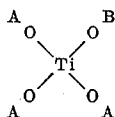
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It was reported that ethylene glycol and 2-ethyl-1,3-hexanediol had a greater tendency to chelate than the 2,3-butanediol and the former were postulated as giving the following structure through rather quick termination of polymerization.



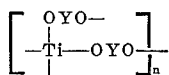
In spite of the uncertainties of the structures of my additive agents, the base oil-compatible-titanium compounds I employ can be either monomeric, polymeric or mixed monomers and polymers. These materials can be produced through reaction, with or without heating, of about $\frac{1}{2}$ to 4 moles of glycol with each mole of titanium tetraester, preferably about 2 to 4 moles of glycol per mole of titanium tetraester. The first product obtained can be employed as such or polymerized through heating or through water addition and heating with there being no particular critical limitation on either, except, of course, the temperature should not be so high as to decompose the desired reaction products. Ordinarily, the polymerization temperature will be above 25° C. and preferably at least about 40° C. When employing heat to obtain a polymer in the absence of water and from a monomer dissolved in solvent, it may be desirable to use a vacuum, say about 5–10 mm. Hg, and a temperature of about 130 to 170° C. to remove the solvent while forming the polymer. Of course, other conditions of temperature and pressure could be employed. If water be present during polymerization, I usually employ at least one part per part of titanium reactant ester, with 2 to 20 parts of water being used most advantageously. At the end of the reaction alcohol and water can be boiled off or otherwise removed. The length of time the heating is conducted can be varied widely and is not critical, and apparently during polymerization non-chelated groups of the titanium reactant are hydrolyzed from the molecule.

The structure of my additive agents might be defined as the base oil-compatible materials of the following formula

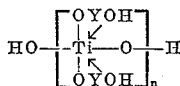


wherein A is hydrogen, a hydrocarbon radical of a titanium tetraester, or B; and B is a glycol hydrocarbon radical containing a glycol hydroxy group. As stated the base oil-compatible polymers formed from such materials are useful.

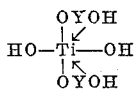
A proposed structure for such polymers formed by heat alone is



When the polymer is made by heating in the presence of water the structure might be



However, the product obtained by heating in the presence of water may not be a true polymer but rather composed of a plurality of



molecules associated by hydrogen bonding. The product may be of some other structure. Y and n in the above formulas have the significance previously given.

Several of my additive agents have been made avail-

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able by E. I. du Pont de Nemours & Company. For instance, they offer for sale materials of the following table:

Table I

REACTANTS

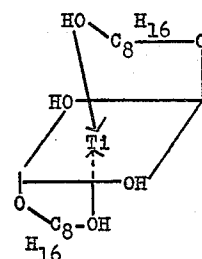
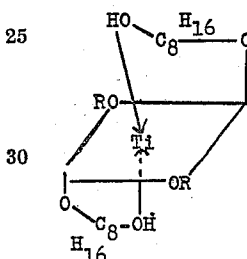
Octylene Glycol Titanates	Molar Proportions		Solvent	Appearance
	Octylene Glycol ¹	Tetra-butyl Titanate		
OGT-21-----	2	1	24% Butanol..	Solid.
OGT-2.21-----	2.2	1	25% Butanol..	Tacky Solid.
OGT-31-----	3	1	28% Butanol..	Liquid.
OGT-41-----	4	1	31% Butanol..	Do.
OGT-21 (washed)-----	2	1	43% Cyclo-hexane.	Solid.
OGT-2.21 (washed)-----	2.2	1	42% Cyclo-hexane.	Tacky Solid.

¹ 2-ethyl-1,3-hexanediol.

The formulas proposed by the manufacturer for these materials are chelated monomers and are as follows:

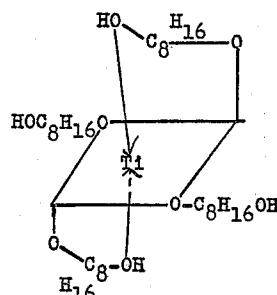
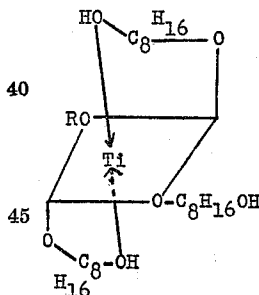
OGT-21

OGT-21 (washed)



OGT-31

OGT-41



wherein R is a butyl radical. These monomers or their base oil-compatible polymers can be employed as extreme pressure additives in my base oils.

The structures of polymeric materials formed from the OGT products by heating alone and by heating in the presence of water have been studied by infrared and X-ray diffraction methods. In these studies three products were used and these were

(a) Prepared by heating OGT-41 to 200° F. in the presence of water (Example VI below);

(b) Prepared by heating OGT-41 to 250° C. in the absence of water (Example VII below); and

(c) Prepared by heating OGT-21 to 250° C. in the absence of water (Example VIII below).

By infrared analysis, product (a) showed a strong absorption peak at 3 microns which is characteristic of a hydroxyl group. The intensity of the peak indicated a hydroxyl number of about 460. The hydroxyl groups apparently were derived by removal of unchelated glycol residues from the OGT-41 in the presence of water. By infrared neither product (b) nor (c) exhibited a hydroxyl number and these products appeared to be similar.

X-ray diffraction analysis of product (a) gave a peak having an intensity of 230 at 15.2 Angstroms. The crystal size was 56 Angstroms and the product was almost amorphous. The principal scattering atom in the prod-

ucts (a), (b) and (c) is titanium. Since all of these products gave but one major diffraction line, it was considered that this was the titanium to titanium distance. Thus product (a) indicated about four such distances. Products (b) and (c) were more crystalline with the former having a major peak at 11.8 Angstroms (intensity 350) and the latter having the same at 12.1 Angstroms (intensity 800). Product (b) exhibited a crystal size of 130 Angstroms corresponding to about eleven titanium to titanium distances and product (c) showed a crystal size of 220 Angstroms or about eighteen such distances.

As previously stated, my extreme pressure agents may vary from liquid to solid as long as they are compatible with the base oil. Frequently, when the titanium additive is in polymeric form the molecular weight will be from about 800 to 3000 and preferably about 1000 to 1800, but the molecular weight may even be as high as 5,000 to 15,000 or 20,000 or more. Advantageously, I employ the low molecular weight polymers as they do not tend to thicken the base oil. The low molecular weight polymer additives frequently have viscosities at 100° F. ranging from about 0.575 to 0.85 cs. on the basis of 1 gram in 40 grams of toluene.

My compositions contain sufficient of the titanium additive agent to increase materially the load carrying capacity of the base oil. Generally, the final lube composition will contain from about 0.001 to 5 weight percent of the additive agent and I prefer about 0.1 to 2%. More than 5% could be used but there does not appear to be any necessity for this. The actual amount of agent employed may be dependent upon the degree of improvement desired and upon factors such as the character of the base oil and the other materials which may be added to or be present in the lubricant composition. For instance, one specification now of interest requires that the lubricant carry at least 3000 lbs. in the Ryder Gear Test Machine, and this value has been far exceeded by providing as little as 0.028 weight percent of titanium in a mineral oil base lubricant through addition of 0.2% of an OGT-41 polymer, see blend No. 4 of Table VIII below. This shows that lesser amounts of the additive could be employed without failing this particular load carrying test.

It has been found that variations in the amount of additive or titanium supplied to synthetic base lubricants, for instance diester oils, can significantly influence the degree of improvement in their load carrying properties. Thus, the addition to several essentially dibasic acid-free diester synthetic oils of 0.2% of my titanium agent, in the form of a 20% OGT-41 polymer concentrate in Plexol 201 (Plexol 201 contains about 0.02% of free sebacic acid which has the formula $\text{COOH}(\text{CH}_2)_8\text{COOH}$), produced compositions which although improved in extreme pressure properties did not satisfactorily carry 3000 lbs. in the Ryder test machine. However, when 1% of OGT-41 polymer was added to an essentially dibasic acid-free di-2-ethyl-hexyl sebacate base composition, the oil had a load carrying ability of about 5000 lbs. in the test.

It has been found that the degree of improvement in the load carrying properties of my lubricating oils, particularly synthetic oils such as the diester oils, afforded by incorporation of my titanium additives, can be materially enhanced by providing in the composition a small but effective amount of a free, base oil-compatible dibasic acid. Generally, the compatible acids I use have molecular weights of up to about 600 which includes for instance monomer and dimer acids. Thus, I can employ at least about 0.005 weight percent of a dibasic acid, preferably having from 2 to about 12 or 20 carbon atoms, in these lube compositions and obtain improved extreme pressure properties, particularly when the amount of titanium additive is such that the composition contains up to about 0.1 weight percent of titanium, preferably up to about 0.05 weight percent of titanium. Of course, the dibasic acid could be present when the lubricant contains more than about 0.1 weight percent of titanium should it be consid-

ered desirable or convenient. In my preferred embodiment the free dibasic acid is about 0.01 to 0.1 weight percent of the composition, and generally there seems to be little if any benefit to be derived from using more than about 1% of the acid when it is added primarily to enhance the effectiveness of the titanium additive. Although the dibasic acids have been found to be useful along with my titanium additives the same result has not been obtained by incorporation of the monobasic acid, decanoic acid, or the half ester prepared from 2-ethyl-hexanol and sebacic acid. The use of the small amount of dibasic acid to enhance the action of the titanium additives towards imparting improved load carrying characteristics to my base oils is particularly desirable where the amount of improvement wanted cannot be obtained by employing the titanium additive alone without using an amount of the latter which contributes to the final lubricant composition another characteristic which is deleterious in a given situation. For instance, there is some indication that when a Plexol 201 base lubricant containing phenothiazine and a silicon anti-foaming agent has incorporated in it more than about 0.05 weight percent of titanium in the form of an OGT-41 polymer the composition exhibits lead and magnesium corrosion properties to an extent which at this time seems undesirable for high temperature jet engine use.

It is sometimes advantageous to ship and handle the additive as a concentrate in the base oil, and thus the agent may be as high as about 75% of such a concentrate but normally the concentrate would contain about 15 to 60% additive. My additive monomers and the polymers made by heating in the presence of water can be blended with the base oil at room temperature but slight heating is preferred when blending this polymer. Polymers made by heating the monomers in the absence of water seem more difficult to blend and temperatures of at least about 150° F. are generally employed during blending of these materials. My compositions can also contain additional agents such as anti-oxidants, anti-foaming additives, corrosion inhibitors, V.I. improvers, other extreme pressure agents, thickeners and other agents added to give desired properties. However, certain agents may decrease the effectiveness of my titanium additives, and this has been found to be the case in instances when my composition contained tricresylphosphate and the OGT-41 polymer. the titanium additives of this invention exhibit anti-foaming activity.

The base oils of my compositions are the mineral or synthetic oils of lubricating viscosity. Preferably, the synthetic oils consist essentially of carbon, hydrogen and oxygen, with or without silicon. Various of these lubricating materials have been described in the literature and generally their viscosity ranges from the light to heavy oils e.g. about 50 SUS at 100° F. to 250 SUS at 210° F. and preferably 30 to 150 SUS at 210° F. Included among the preferred synthetic lubricants are, for example, the polyalkylene glycols prepared from alcohols and alkylene oxides. A number of these oils are available as Ucons prepared from aliphatic alcohols and propylene oxide and having molecular weights of about 400 to about 3000. Related lubricants are the higher molecular weight alkylene oxides, polycarbonates, Acryloid polymers, formals, polyformals, polyglycidyl ethers and other ethers. The oils containing silicon include the polysiloxanes of lubricating viscosity, particularly the polymethyl, polyethyl and polyphenyl siloxanes, for instance of 200 to 1000 or more molecular weight.

Widely employed synthetic lubricating oils are the ester types, for instance the mono- and diesters, and these are the base oils I prefer. The esters are made from alcohols and either mono- or polycarboxylic acids. Among the dicarboxylic acids employed are those of 2 to 12 carbon atoms, particularly the aliphatic acids such as adipic, azelaic, suberic, alkenyl succinic, sebacic, etc. Preferred monocarboxylic acids are those of 8 to 24 carbon atoms

such as stearic, lauric, etc. The alcohols employed usually contain less than about 20 carbon atoms and are generally aliphatic, such as the butyl, hexyl, 2-ethylhexyl and dodecyl alcohols. The alcohols can also be polyfunctional materials, such as glycols, and included among the glycols are the ether glycols. Various ester base oils are disclosed in United States Patents Nos. 2,499,983; 2,499,984; 2,575,195; 2,575,196; 2,703,811; 2,705,724 and 2,723,286. As I have mentioned my preferred lubricating base oils are synthetic and consist essentially of carbon, hydrogen and oxygen with or without silicon, i.e. the essential nuclear chemical structure is formed by these elements. However, these oils may be substituted with other elements such as halogens, e.g. chlorine and fluorine.

Among other specific synthetic oils falling within the above classes are ethyl palmitate, ethyl stearate, di-(2-ethylhexyl) sebacate, ethylene glycol di-laurate, di-(2-ethylhexyl)phthalate, polymethyl siloxane of 149 SUS viscosity at 210° F., 1-naphthyl cetyl ether, dicetyl ether, polypropylene glycol (and mono- and diethers) (m.w. 600), di-(1,3-methyl butyl) adipate, di-(2-ethyl butyl) adipate, bis(1H,1H,7H-dodecafluoroheptyl)-3-methyl glutarate, di-(1-ethyl propyl) adipate, diethyl oxylate, glycerol tri-n-octoate, di-cyclohexyl adipate, di-(undecyl) sebacate, tetraethylene glycol-di-(2-ethylene hexoate), di-cellosolve phthalate, butyl phthalyl butyl glycolate, di-n-hexyl fumarate polymer, dibenzyl sebacate, diethylene glycol bis(2-n-butoxy ethyl carbonate) and oxo process alcohols such as isocetyl, isodecyl and isotridecyl alcohols made from branched chain propylene polymers.

In preparing the polymer additives I prefer to take one part by weight of OGT-41 and 3 to 6 parts by weight of water and heat the mixture to at least about 60° C. while agitating. The temperature is held for about 15 to 30 minutes and agitation is then stopped. A white, sticky, insoluble, elastic polymer settles while octylene glycol and butanol solvent form an upper layer. The top layer and the water are decanted and the polymer is water washed and blended with the base oil, for instance, to give a concentrate of about 15 to 60 weight percent of polymer. The mixture is settled and the water layer separated. The oil is then heated to remove remaining water and butanol. The polymer could be preheated to remove water and solvent before addition to the base oil in any concentration.

My monomer additives can be dissolved in a silicone oil; however, difficulty has been experienced in this respect when using the polymers. Thus in the latter case, it has been found to be advantageous to dissolve the monomer; e.g. OGT-41, in the silicone, preferably as a concentrate; and then heat the mixture, for instance, to about 300° F., to remove the alcohol formed during the polymerization. The polymer so formed will remain compatible with the silicone oil even when the concentrate is combined with additional base oil to prepare the lubricant.

The following examples serve to illustrate the preparation of my additive polymers and their addition to base lubricating oils.

EXAMPLE I

2520 grams of OGT-21 were mixed at 88° F. with 4000 grams of water. After stirring for 1 hour at about 75 to 88° F., the material was filtered through paper to separate the solid polymer which had been formed. The crude polymer analyzed 10.35 weight percent ash and 6.20 weight percent titanium. 1235 grams of the crude polymer were added to 2000 grams of Plexol 201. The solution was heated to 150° C. on a hot plate for 10 minutes which gave an additive concentrate analyzing:

Wt. percent ash	8.68
Wt. percent titanium	5.20
Acid No., ASTM-D974	4.17
Viscosity, centistokes at 210° F.	3.749

EXAMPLE II

150 grams of OGT-41 were added to 300 grams of water. The mixture was agitated and heated at 212° F. for 30 minutes. The liquid was decanted from the solid product at room temperature. The polymer was air dried and the product weighed 51 grams.

EXAMPLE III

773 grams of OGT-41 were placed in a 6-liter beaker. Four liters of deionized water were poured in with vigorous stirring by hand. A milky, yellow suspension formed. The mixture was heated and stirred. After about 5 minutes the temperature reached 28° C. and a white, tacky precipitate formed. After a total of 30 minutes when the temperature reached 55° C. the product took on a curdy appearance. At 65° C. there were three components present; a white, heavy, tacky precipitate; a clear solution and a yellow, only curdy material. The desired product (the white, heavy, tacky precipitate) was separated by decantation and filtration. The solid on filter paper was left in air overnight and then was stored in a desiccator for 20 hours. 134 grams of product were obtained and the product analyzed 25.6 weight percent ash, which is equivalent (by calculation) to 15.3 weight percent titanium.

EXAMPLE IV

2555 grams of OGT-41 were added with stirring to 3000 grams of water. The mixture was heated and held at 80° C. for 1 hour. Upon standing the reaction mixture separated into three layers and the liquid organic and aqueous layers were decanted to give 835.0 grams of crude polymer. This polymer analyzed:

	Weight percent
Titanium	11.15
Carbon	48.65
Hydrogen	9.29

An additive concentrate was formed by mixing 819 grams of the crude polymer with 800 grams of Plexol 201 and heating the mixture at 135° C. for 15 minutes. The resulting additive concentrate analyzed:

	Weight percent
Ash	10.44.
Viscosity, centistokes:	
At 100° F.	29.84.
At 210° F.	5.01.
Acid No., ASTM-D974	5.4.
Pour point, ° F.	below -80.

EXAMPLE V

500 grams of OGT-21 (washed) were mixed at room temperature with 2000 grams of water while stirring. The temperature of the mixture was increased to 100° C. and held for 18 hours. A white polymer formed. The reaction mixture was cooled and the solid product recovered by filtration. The product was air dried at room temperature for 24 hours and analyzed:

Wt. percent ash	21.9
Wt. percent titanium	13.1
Wt. percent carbon	46.28
Wt. percent hydrogen	9.41

EXAMPLE VI

100 grams of OGT-41 were mixed with 200 grams of water. The mixture was heated at 200° F. for 1 hour and then filtered. The filtered solid product was washed with 200 grams of hot water and then air dried for 24 hours. The dried product analyzed:

Wt. percent ash	28.39
Molecular weight, benzene boiling point method	1316

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EXAMPLE VII

A polymer was made by heating 100 grams of OGT-41 to 250° C. and holding this temperature for 5 minutes.

EXAMPLE VIII

A polymer was made by heating 100 grams of OGT-21 to 250° C. and holding this temperature for 5 minutes. It was more difficult to dissolve this polymer in Plexol 201 than the preferred polymers formed in the presence of water. At 350° F., 150 ml. of Plexol 201 were required to dissolve ½ gram of the polymer of this example.

EXAMPLE IX

7200 grams of OGT-41 were mixed with 8000 grams of water in a stainless steel beaker. The mixture was agitated while increasing the temperature to 95° C. where it was held for 20 minutes. Afterwards the mixture stood at room temperature for 12 hours and the liquid was decanted from the white polymer which had been formed. 7000 grams of water were then added to the polymer and the mixture was heated to 80° C. This temperature was held for 2 hours while agitating the mixture. The temperature was then allowed to drop to room temperature and the reaction mixture stood for 12 hours. The liquid was decanted and the polymer product was dried for 24 hours on paper at 25° C. and 50% relative humidity. The product weighed 2640 grams, had an ash of 25.8 weight percent and a molecular weight in benzene by boiling point method of 1314.

EXAMPLE X

2640 grams of polymers were prepared by combining three separate products, each obtained according to the following procedure. 7.2 parts of OGT-41 were mixed with stirring with 6 parts of water. The mixture was heated about 30 minutes at 180° F. and it then stood overnight. A clear supernatant organic liquid and the water layer which had been formed were decanted from the resulting polymer. Nine parts of water were then added to the polymer and after heating and stirring for 30 minutes at 180° F. the mixture was allowed to settle for 16 hours. The liquid phases were decanted and the polymer transferred to filter paper and air dried for 24 hours at 25° C.

EXAMPLE XI

An additional amount of polymer was prepared by the method of Example X and the products were combined to provide 2920 grams of air dried polymer. The polymer was then blended with 4735 grams of Plexol 201 to give an additional concentrate. Blending was accomplished by heating the titanium polymer in the Plexol 201 for 30 minutes at 160° F. and then filtering through paper. This concentrate analyzed:

	Weight percent
Ash	1078.
Viscosity centistokes:	
At 100° F.	29.58.
At 210° F.	5.02.
Acid No., ASTM-D974	6.62.
Pour point, ° F.	below -80.

EXAMPLE XII

2000 grams of OGT-2.21 were mixed while stirring with 4000 grams of water. The mixture was heated and held at 75° C. for 40 minutes. The aqueous and organic liquid layers were decanted from the polymer which had been formed and the crude polymer analyzed 16.1 weight percent titanium.

EXAMPLE XIII

2000 grams of OGT-41 were mixed while stirring with 6000 grams of water. The mixture was heated and held

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at 60° C. for about 16.65 hours. The aqueous and organic liquid layers were decanted from the polymer which had been formed and the polymer was air dried for 24 hours at 25° C. The resulting material analyzed:

	Weight percent
Titanium	16.9
Carbon	50.05
Hydrogen	9.30

EXAMPLE XIV

Ten liters of OGT-41 were placed in a 40-liter stainless steel beaker. To this were added 30 liters of distilled water with agitation, and the mixture was heated at 80° C. for three hours with stirring. The agitation and application of heat were stopped, and the contents of the beaker were allowed to cool to 25° C. At this point the butanol solvent and water (liquid layer) were decanted from the white precipitate of polymer. Thirty liters of distilled water were added and the temperature was increased to 80° C. with good agitation. The application of heat was stopped and the product was allowed to settle for four hours. Then water and solvent were decanted, and the polymer was dried for 60 hours at room temperature (25° C.) at about 30% relative humidity. The yield of air dried titanium polymer was about 38%. Analysis of the polymer was:

Wt. percent titanium	13.5
Wt. percent ash	22.56
Acid No., ASTM-D974	21.3
Molecular weight	12,800
Initial pH of material	7.6

EXAMPLE XV

164 pounds of OGT-41 were weighed into a stainless steel Pfaudler kettle. While stirring vigorously, 210 pounds of tap water were added. The stirred mixture of water and precipitated polymer was heated to 170° F. over a twenty-minute period. When the mixture reached 170° F., the agitation was stopped, and the mixture was allowed to settle 1 hour. The upper organic layer and water were siphoned off the wet polymeric white solid. A second charge of tap water, 210 pounds, was added to the kettle, while agitating vigorously, and the mixture was heated to 170° F. The agitation was stopped, and the mixture was allowed to settle two hours. The bulk of the water was siphoned off the polymer; the last part of the water was drained through the wet granular polymer to the bottom valve on the kettle and discarded. 147 pounds of Plexol 201 were then charged to the stirred kettle, and the contents heated to 180° F. At about 180° F., the polymer was dissolved. The agitation was stopped, and the solution settled for 30 minutes. The lower water layer was drawn off, and discarded. At this point the organic layer was almost clear, except for a slight water haze. The organic layer was dehydrated by heating to 250° F. and cooled to 80° F. Product yield was 190 pounds of clear yellow liquid, having the following analysis:

Kinematic viscosity	
At 100° F., cs.	16.47
At 210° F., cs.	3.691
Titanium, wt. percent	3.20
Acid number (ASTM-D974)	3.10
Approximate additive concentration, wt. percent	20.0

In the table immediately below, several tests on synthetic lube oil compositions are presented. Compositions 1 through 5 fall within the present invention while composition 6 not containing my additive is included for comparative purposes to show the improvement in load carrying capacity afforded by my titanium additive agents.

Table II

	1	2	3	4	5	6
Composition, Wt. Percent:						
Plexol 201 ¹	99	99	99.18	97.57	98.5	Balance.
Phenothiazine ²	0.5	0.5	0.5	0.5	0.5	0.5
D.C.F. 200-60,000 ³	0.001	0.001	0.001	0.001	0.001	0.001
Titanium Polymer Concentrate Preparation	0.5	0.5	0.32	1.93		
Polymer Preparation	Ex. II	Ex. III	Ex. VI	Ex. I		
OGT-41					1.0	
Tests:						
Viscosity at:						
-65° F., cs.	8,730	8,705	9,069	9,124	8,843	
100° F., cs.	12.91	12.91	12.86	12.85	12.75	
210° F., cs.	3.357	3.358	3.367	3.345	3.314	3.6
Viscosity Index	152.3	152.8	155.4	151.9	150.1	
Pour, ° F.	below -80	below -80	below -80	below -80	below -80	
Acid number, ASTM-D 974	0.15	0.08	0.07	0.15	0.46	
Ryder Gear, pounds	5,600+	4,400	5,600+	5,600+	5,600+	2,100.

¹ A di-ethylhexyl sebacate oil having a kinematic viscosity at 100° F. of 12.3 centistokes, a viscosity index of 154, a pour point of below -80° F. and acid number of 0.12.

² Phenothiazine is an anti-oxidant.

³ D.C.F. 200-60,000 is a methyl silicone polymer having a viscosity of 60,000 cs. at 25° C. and is an anti-foaming agent.

The above data clearly illustrate that in the presence of a dibasic acid my titanium additive monomers or polymers effectively increase the load carrying capacity of the synthetic base oils. Thus, compositions 1 to 5 frequently gave load carrying ratings of 5600+ on the Ryder test machine. As 5600 is the capacity of this machine, such readings do not, of course, indicate the ultimate load carrying capacity of the lubricant tested. The extreme pressure characteristics of these compositions are vastly improved over a similar synthetic lube oil composition containing no titanium additive where the composition had a rating on the Ryder machine of only about 2100 pounds, see composition 6 of Table II. A tentative proposed military specification requires a minimum Ryder rating of 3000 pounds which illustrates an inadequacy of the base oil composition not containing my titanium additive.

The data of Table II show that in the presence of the dibasic acid my extreme pressure agents can be added in very small amounts and still exhibit outstanding load carrying improvement, for instance see the tests on composition 3. Thus, any slightly deleterious properties which might be imparted by the additives are readily overcome. For instance, there has been some indication that the used oil-acid number increase of certain of my composition is somewhat above the proposed tentative military specification, this was true with composition 2 of Table II. On the other hand, since in the presence of the dibasic acid the additive exhibits such outstanding properties at low concentration, passage of corrosion and oxidation tests is assured merely by decreasing the amount of additive employed or by addition of small amounts of compensating additives such as anti-oxidants etc. Acid number increase and other minor unwanted characteristics imparted by my titanium additive agents thus are not serious problems to their commercial utilization. Of course, whether or not various characteristics are consid-

ered to be disadvantageous is a function of the specifications to be met.

Tests on a series of lubricating oil blends have been conducted to show the effect of varying the amount of my OGT polymer titanium additive present in a substantially dibasic acid-free diester base oil. The pertinent data from these tests are as follows:

Table III

	Blend No.		
	1	2	3
Composition, weight percent:			
Di-2-ethylhexyl sebacate (acid-free) ¹	99.5	balance	balance
Phenothiazine	0.5	0.5	0.5
D.C.F. 200-60,000	0.0005	0.0005	0.0005
Titanium Polymer of Example XIV			1.0
Titanium Polymer Concentrate of Example XV		1.0	
Tests:			
Acid No. ASTM-D 664	0.02	0.09	0.07
Wt. Percent Titanium		0.037	0.133
Ryder Gear, pounds	1,760, 1,760	2,170, 2,430	4,980, 5,130

¹ Acid-free material was prepared by clay contacting Plexol 201.

The data of Table III show that with a dibasic acid-free diester oil, the addition of 0.037% titanium as an OGT-41 polymer concentrate in Plexol 201 (blend No. 2) provided improvement in load carrying properties; however, the composition did not satisfactorily carry 3000 pounds. When the amount of OGT-41 polymer added was increased to provide 0.133% titanium as in blend No. 3, the composition exhibited extreme pressure characteristics sufficient to carry around 5000 pounds in the Ryder gear test machine.

The effects of adding free dibasic acid and other selected materials to blend No. 2 of Table III were determined in a series of tests which are reported in Table IV.

Table IV

	Blend No. 2 Table III	Blend No.					
		1	2	3	4	5	6
Composition, weight percent:							
Di-2-ethylhexyl sebacate (acid-free as in Table III)	balance	balance	balance	balance	balance	balance	balance
Phenothiazine	0.5	0.5	0.5	0.5	0.5	0.5	0.5
D.C.F. 200-60,000	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
Titanium Polymer Concentrate of Example XV	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sebacic Acid (COOH(CH ₂) ₈ COOH)		0.01	0.02	0.03			
Adipic Acid (COOH(CH ₂) ₄ COOH)					0.02		
Decanoic Acid						0.3	
Half ester of 2-ethylhexanol and sebacic acid							0.1
Tests:							
Acid No. ASTM-D 664	0.09	10.15	0.21	0.24	0.13	0.15	0.16
Wt. Percent Titanium	0.037	0.032	0.032	0.029	0.027	0.028	0.028
Ryder Gear, pounds	2,170, 2,430	3,030, 2,740	4,870, 3,820	3,990, 4,270	3,725, 4,200	2,460, 2,240	2,900, 2,140

¹ Calculated.

These data illustrate that the provision of free-dibasic acid in the diester oil containing my titanium additive enhances the load carrying properties of the composition. Also, in these tests the addition of decanoic acid or the half-ester of 2-ethylhexanol and sebacic acid did not provide a similar effect.

The results of the tests of Table IV are confirmed by the following data of Table V obtained with respect to two different diester base oils.

Table V

	Blend No.					
	1	2	3	4	5	6
Composition, weight percent:						
Emolein 2958 ¹	balance	balance	balance	balance	balance	balance
Di-2-ethylhexyl adipate ²	0.5	0.5	0.5	0.5	0.5	0.5
Phenothiazine	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
D.C.F. 200-60,000						
Titanium Polymer Concentrate of Example XV	1.0	1.0	1.0		1.0	1.0
Sebacic Acid		0.03	0.1	0.03		0.03
Tests:						
Acid Number, ASTM-D 664		0.31	0.70	0.19	0.10	0.19
Wt. Percent Titanium	0.031	0.033	0.033		0.031	0.03
Ryder Gear Load	2,030, 2,100	4, 510, 3,760	3,515, 4,060	2,050, 2,380	1,390, 1,240	3,470, 3,590

¹ Di-2-ethylhexyl azelate having no free acid, Acid No.=0.0.

² Base oil had no free acid, Acid No.=0.01.

Data have been obtained which show that certain additive materials can decrease the effectiveness of my titanium agent. The data of Table VI illustrate this point.

Table VI

	Blend No.	
	1	2
Composition, weight percent:		
Plexol 201	Balance	
Phenothiazine	0.5	
D.C.F. 200-60,000	0.0005	
Titanium Polymer of Example XIV	0.464	
Tricresylphosphate		4.0
Tests:		
Wt. Percent Titanium, approx.	0.03	0.03
Ryder Gear, pounds	4,345, 5,500+	2,870, 2,870

Thus, the addition of tricresylphosphate, along with my OGT polymer titanium agent, to a diester base oil containing free sebacic acid materially decreased the extreme pressure properties of the lubricant. Tricresylphosphate is a widely used extreme pressure agent.

As previously indicated the compositions of this invention can contain agents other than the base oil and my titanium additives. As an example various organic or inorganic thickeners can be added and if desired sufficient of the thickener can be used to provide a lubricant of grease consistency. A grease of good color, body and load carrying capacity can be made by adding 10 weight percent of lithium stearate and 0.5 weight percent of the polymer of Example X to Plexol 201. The base oil of such greases can also be comprised of mineral lubricating oils and synthetic-mineral oil blends.

To illustrate that my titanium additives can impart increased load carrying capacity even to thickened lubricants a composition was prepared containing 72.7 weight percent Plexol 201, 26 weight percent of an ester thickener, 0.5 weight percent phenothiazine, 0.001 weight percent D.C.F. 200-60,000, and 0.8 weight percent of the polymer concentrate of Example IV. The ester thickener was prepared by charging to a 50-liter flask equipped with a metal paddle, stirrer, azeotrope trap and condenser having a thermocouple extending into the flask contents, 12,120 grams of sebacic acid, 9,000 grams of polypropylene glycol 150, 7,000 grams of xylene and 110 grams of paratoluene sulfonic acid. The solution was reacted a total of 10 hours at temperatures ranging

from 225 to 312° F. during which time 1906 grams or about 88% of the theoretical water of the esterification reaction were collected. To the resulting mixture 2105 grams of 2-ethyl-hexyl alcohol were added and the mixture was heated 5.5 hours with the collection of 175 grams of water. The final reaction flask temperature was 330° F. and total amount of water collected at this stage represented 96.5% of theoretical. The xylene carrier was stripped from the reaction mixture and the

bottoms charged to a pressure autoclave. 4.21 pounds of propylene oxide were added to the autoclave to take care of 42.1 lbs. of the polyester which had not yet been completely neutralized. The autoclave was swept free of air by nitrogen. The autoclave was then heated to 344° F. and kept at this temperature for 7¼ hours. The initial pressure was 65 p.s.i.g. and by the end of 7¼ hours it had dropped to 60 p.s.i.g. The mixture was allowed to stand overnight and on the following day was maintained at reaction temperature for 6½ hours while stirring. The propylene oxide was flashed off and the product analyzed: Acid No. ASTM-D974, .05; viscosity at 210° F. centistokes 74.00.

The resulting composition containing the ester thickener and my titanium additive had a viscosity at 210° F. of 8.139 centistokes and in the Ryder gear machine gave load carrying capacities of 5260 and 4450 lbs. In the case of a similarly thickened fluid in which my titanium additive concentrate was replaced with an additional amount of Plexol 201 (giving a total Plexol 201 content of 73.5 weight percent), the product had a viscosity at 210° F. of 8.111 centistokes and on the Ryder gear test machine indicated a load carrying capacity of 3440 and 3530 lbs. From these data it is seen that my titanium additive increased the load carrying capacity of the ester thickened lubricant about 900 to 1800 lbs. on the Ryder test machine.

My titanium-containing extreme pressure additives can also be employed in lubricating oils comprised of blends of a synthetic base oil and a mineral lubricating oil. These blends can contain any desired amounts of the separate oils, as an example it might be desirable to use a blend having as little as about 1 to 10 volume percent of the synthetic oil. Three tenths weight percent of the polymer of Example X and 5.0 weight percent of Plexol 201 were incorporated in a Mid-Continent petroleum, solvent treated neutral oil having a viscosity of 50 to 55 SUS at 100° F. and a viscosity index of 95. This composition along with a blend of the mineral oil with 5 weight percent Plexol 201 containing no titanium additive were tested in the Timken L-20 Weedout procedure for 16 hours at 100 pounds load, 200° F. and 200 r.p.m.'s. The titanium-containing composition gave a total test cup and block wear of only 34.4 milligrams. The cup and block were bright and polished and the absence of ridging evidenced a lack of surface fatigue. The composition containing only the mineral oil and Plexol 201 failed in one minute after the break-in period

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and the test was stopped. The break-in was run for 30 minutes at 200 r.p.m.'s and 50 pounds load with the fluid starting at room temperature.

The effectiveness of my extreme pressure additives in mineral lubricating oils was illustrated in a series of tests reported in Table VIII.

Table VIII

	Blend No.			
	1	2	3	4
Composition, weight percent:				
Mineral Oil Base	100	99.0	99.6	99.8
Titanium Polymer of Example XIV			0.4	0.2
Titanium Polymer of Example X		1.0		
Tests:				
Acid No. ASTM-D 664	0.01	0.13	0.07	0.09
Wt. Percent Titanium		0.17	0.055	0.028
Ryder Gear, pounds	2,430 2,390	5,400 5,120	3,800 3,800	4,600 4,710

¹ Base mineral oil contained 72 volume percent of 600 SUS at 100° F. solvent treated Mid-Continent neutral oil and 28 volume percent of 200 SUS at 100° F. solvent treated Mid-Continent neutral oil; the blend has a viscosity of about 450 SUS at 100° F.

In a composition containing 0.08 weight percent of Emery's dimer of linoleic acid, 0.2 weight percent of the titanium polymer of Example XIV, and the balance being the mineral oil base of Table VIII, the Ryder gear rating was about 4900 pounds. Thus, the presence of the compatible dibasic acid in the mineral oil base gave some improvement in load carrying properties of the oil containing my titanium additive in an amount to afford about 0.03 percent titanium.

This application is a continuation-in-part of my application Serial No. 579,140, filed April 19, 1956, and now abandoned.

It is claimed:

1. A composition consisting essentially of a base oil of lubricating viscosity, a sufficient amount to enhance the load carrying capacity of an additive material selected from the group consisting of base oil-compatible products formed by the reaction of a titanium tetraester with a glycol containing from 2 to about 24 carbon atoms, said titanium tetraester and glycol reacting in the ratio of about ½ to 4 moles of glycol to each mole of titanium tetraester, and the base oil-compatible polymers thereof, and an amount of a base oil-compatible dibasic acid sufficient to provide increased load carrying capacity to the composition.

2. The composition of claim 1 in which the glycol is a 1,3-diol.

3. The composition of claim 1 in which the titanium additive material is about 0.1 to 2 weight percent of the composition.

4. The composition of claim 1 in which the titanium additive material is a titanium tetraester-glycol polymer formed by heating in the presence of water.

5. The composition of claim 1 in which the titanium additive is in an amount to provide up to about 0.1 weight percent of titanium and in which there is present about 0.005 to 1.0 weight percent of the dibasic acid.

6. The composition of claim 1 in which the base oil is a diester.

7. The composition of claim 6 in which the titanium content is up to about 0.05% by weight of the composition and the dibasic acid is about 0.01–0.1% by weight of the composition.

8. The composition of claim 6 in which the dibasic acid has 2–12 carbon atoms.

9. The composition of claim 8 in which the reaction is with about 2 to 4 moles of a glycol containing about

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5–12 carbon atoms to each mole of titanium tetraester, and in which the titanium content is up to about 0.1% by weight of the composition and the dibasic acid is about 0.01–0.1% by weight of the composition.

10. The composition of claim 9 in which the titanium content is up to about 0.05% by weight of the composition and the dibasic acid has the formula $\text{COOH}(\text{CH}_2)_n\text{COOH}$ where n is a number from 4 to 8.

11. The composition of claim 10 where the glycol is a 1,3-diol.

12. The composition of claim 11 where the base oil is di-(2-ethylhexyl)-sebacate.

13. A composition consisting essentially of a diester synthetic organic base oil of lubricating viscosity and a sufficient amount to enhance the load carrying properties of an additive material selected from the group consisting of base oil-compatible products formed by the reaction of a titanium tetraester with a glycol containing from about 5 to 12 carbon atoms, said titanium tetraester and glycol reacting in the ratio of about 2 to 4 moles of glycol to each mole of titanium tetraester, and the base oil-compatible polymers thereof, and an amount of a base oil-compatible dibasic acid sufficient to provide increased load carrying capacity to the composition.

14. The composition of claim 13 in which the glycol is a 1,3-diol.

15. The composition of claim 13 in which the titanium additive material is about 0.1 to 2 weight percent of the composition.

16. The composition of claim 13 in which the titanium additive material is a titanium tetraester-glycol polymer formed by heating in the presence of water.

17. The composition of claim 13 in which the titanium additive is in an amount to provide up to about 0.1 weight percent of titanium and in which there is present about 0.005 to 1.0 weight percent of the dibasic acid.

18. A composition consisting essentially of a diester synthetic organic base oil of lubricating viscosity having added thereto a sufficient amount to enhance the load-carrying properties of a base oil-compatible dibasic acid in the amount of about 0.01 to 0.1% by weight of the total composition and an additive material selected from the group consisting of base oil-compatible products formed by the reaction of a titanium tetraester with a glycol containing from about 5 to 12 carbon atoms said titanium tetraester and glycol reacting in the ratio of about 2 to 4 moles of glycol to each mole of titanium tetraester, and the base oil compatible polymers thereof, in an amount sufficient to enhance the load-carrying capacity and to supply up to about 0.1% by weight of titanium to the total composition.

19. A lubricating composition consisting essentially of di-(2-ethylhexyl)sebacate as the base oil, about 0.1 to 2 weight percent of a base oil-compatible, additive formed by the reaction of a titanium tetraester with 2-ethyl-1,3-hexanediol, said titanium tetraester and diol reacting in the ratio of about 4 moles of diol to each mole of titanium tetraester, said additive being sufficient to supply up to about 0.1% by weight of titanium to the total composition and about 0.01 to 0.1 weight percent of sebacic acid.

20. A lubricating composition consisting essentially of di-(2-ethylhexyl) sebacate as the base oil, about 0.1 to 2 weight percent of a base oil-compatible, additive formed by reacting a titanium tetraester with 2-ethyl-1,3-hexanediol, said titanium tetraester and diol reacting in the ratio of about 4 moles of diol to each mole of titanium tetraester, and then heating the product of this reaction in the presence of water, said additive being sufficient to supply up to about 0.1% by weight of titanium to the total composition and about 0.01 to 0.1 weight percent of sebacic acid.

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