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EXTREME PRESSURE LUBRICATING OILS

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This invention relates to a synthetic lubricant additive material, which when added to synthetic lubricating oils or greases compounded with synthetic oils imparts improved oiliness and extreme pressure characteristics to the lubricant. The invention relates also to synthetic lubricants and particularly synthetic ester type lubricating oils containing this additive material. More particularly, the invention relates to polymerized glycol and polyglycol esters of certain mixtures of dicarboxylic acids and to synthetic lubricating oils, particularly of the ester type, containing these polymerized esters.

With the development of turbo-jet and turbo-propeller engines, the development of lubricants suitable for lubricating the engine parts and auxiliary gear drives associated therewith, has posed a difficult problem, particularly because of the extreme temperature conditions under which lubricants must perform satisfactorily. Moreover, in these engines, it is desired that the same lubricant serve for the antifriction bearings in the engine itself, as well as for the accessory drive gear trains. Thus, a low viscosity oil which must be used in the antifriction bearings has to serve as a lubricant for the gears in other parts of the mechanism. Moreover, it is the tendency at the present time to reduce the weight of gear train assemblies, which means a reduction in gear sizes with consequent increase in gear tooth pressure. Oils which are suitable for the antifriction bearings must have extremely low pour points, e.g., -50 to as low as -100° F., must be sufficiently fluid at temperatures of -65° F., for example, to serve as lubricants for the antifriction bearings at such temperatures and yet not vaporize excessively and must still have lubricating ability at elevated temperatures, e.g., as high as 350 to 500° F. Preferably these oils will have kinematic viscosities of 5 to 20 centistokes at 100° F. For the same oil to be useful in lubricating gear trains, it is essential that the oil has what is referred to in the art as extreme pressure properties or characteristics in order to prevent rupture of the lubricant film under high loads, i.e., high gear tooth pressures with resultant scuffing, galling, or even seizure and welding. Also the lubricant must prevent excessive wear on the rubbing surfaces.

Synthetic ester type lubricants, as for example, di-2-ethyl hexyl sebacate, di-iso-octyl adipate and corresponding esters of various mixtures of dicarboxylic acids are found to have the desirable properties of low pour point, relatively low viscosity at sub-zero temperatures, high flash points together with sufficiently good oiliness characteristics for the lubrication of antifriction bearings in the turbo engines. However, such oils do not have sufficient extreme pressure characteristics to make them suitable for use in the gear trains associated with the turbo engines. Moreover, it has been found that the extreme pressure additives which have in the past been used to impart extreme pressure characteristics to mineral oil and/or synthetic lubricants are not satisfactory additive materials for the synthetic oils to be used in turbo engines because these additive materials are in general

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relatively unstable under the conditions of use and cause corrosion of the lubricated parts. Particularly serious in this respect is the corrosion of copper, silver and their alloys which are present in the lubricating system. These additives include the sulfurized materials, such as sulfurized fatty oils, sulfurized terpenes and the like; chlorinated materials, such as chlorinated organic compounds, as for example dichlorophenylstearic acid, chlorinated paraffin wax and the like; phosphorus containing materials such as the phosphate esters, e.g., tricresyl phosphate; and phosphorus and sulfur containing materials, such as phosphosulfurized hydrocarbons, terpenes and similar materials. Apparently these compounds decompose with the liberation of detrimental and corrosive substances in use in the turbo-jet engines.

It has been found that a particular class of polymerized glycol and polyglycol esters of a particular mixture of dicarboxylic acids produced by the controlled liquid phase oxidation of paraffin wax, when added to synthetic lubricants imparts to such lubricants the desirable extreme pressure and in some instances antiwear characteristics making such lubricants eminently satisfactory for use in the mentioned turbo engines and accessory gear trains.

It has also been found that these polyesters when added to the synthetic lubricants improve the viscosity-temperature characteristics of the lubricants as characterized by the Dean and Davis viscosity index. Thus, they are found to increase the viscosity index of the oils. Moreover, these additives act as pour point depressants in such synthetic oils.

Thus, it is an object of this invention to prepare an additive material suitable for addition to synthetic lubricants of the ester type which additive imparts extreme pressure characteristics as well as improved viscosity index and lowered pour point to such lubricants and it is another object to prepare synthetic lubricating oils having these characteristics.

Another object of the invention is to prepare a polymerized glycol or polyglycol ester of a particular mixture of dicarboxylic acids obtained by the controlled oxidation of paraffin wax, which polymerized ester when added to ester type synthetic lubricating oils imparts extreme pressure characteristics to the oil and to prepare ester type synthetic oils containing this additive material.

A further object of this invention is to prepare polymerized esters of the type described from relatively cheap raw materials.

The above and related objects are accomplished by oxidizing paraffin wax under specific conditions to obtain an oxidized wax having an acid number within the range of 460 to 600 mg. KOH/g., separating from this oxidized wax a fraction consisting primarily of dicarboxylic acids, esterifying the separated fraction of dicarboxylic acids with a glycol or polyglycol as defined hereinbelow under conditions leading to the formation of polymerized esters. The resulting polymerized esters are stable compounds and when added to ester type synthetic lubricants, impart extreme pressure and antiseize characteristics to the oil without reducing the stability of the oil and without adversely affecting pour point, viscosity and flash point characteristics of the oil.

The dicarboxylic acids which are useful in preparing the polymerized glycol and polyglycol esters of this invention are obtained by various separation processes, which will be described later, from paraffin wax oxidized in a certain manner and to a definite degree. It is to be noted that this same fraction of dibasic acids is one which may be employed in preparing the synthetic lubricating oil base to which the polyesters may subsequently be added. Thus, certain monohydroxy aliphatic alcohol esters and certain glycol and polyglycol monoalkyl ether esters of

acid mixtures produced as above described are lubricants per se and may be employed as the base lubricant to which the polymerized glycol or polyglycol esters are added in the preparation of extreme pressure lubricants.

The paraffin wax to be employed in the preparation of the mixed dicarboxylic acids to be used in preparing the esters of this invention is one having a melting point between about 90° F. and about 200° F. and preferably between about 120° F. and about 165° F. It must be relatively oil free and free from asphaltic and resinous materials. Suitable paraffin waxes are obtained from topped waxy residue by extraction with liquefied propane to separate asphaltic materials from the oil and subsequently chilling the deasphalted oil to crystallize wax which may then be separated from the propane-oil solution. The precipitated wax is freed from oil by dissolving it in a solvent such as methyl ethyl ketone and chilling the resulting solution to precipitate an oil-free wax. Such dewaxing and deoiling processes are well known and are described in United States Patent No. 2,229,658. Deoiled waxes obtained by other refining processes using other solvents or combinations of solvents are also satisfactory for use in the oxidation process of this invention. Such waxes comprise predominantly paraffinic and isoparaffinic hydrocarbons having between about 15 and 50 carbon atoms per molecule. Other useable stocks which are useable but which are not to be considered as the full equivalent of the refined paraffin wax described may be obtained by separation of normal paraffins from stove oil, gas oil, or lubricating oil stocks by urea adduction. Straight chain fatty acids, such as stearic or palmitic are also satisfactory charge stocks.

The conditions under which oxidation is effected are important and must be controlled within the limits indicated in order to obtain the particular dicarboxylic acid mixtures having the characteristics and advantages described herein. Oxidation is preferably effected in a stainless steel oxidation chamber although other corrosion-resistant vessels or vessels having corrosion resistant liner may be employed. The vessel must be capable of withstanding the pressures to be employed. In carrying out the oxidation, paraffin wax of the quality described is charged to the oxidation vessel and heated to a temperature between 210° F. and 260° F., the preferred temperature range being 240° F. to 255° F. Preferably a small amount of an oxidation catalyst will be added to the paraffin wax prior to the oxidation and in lieu of adding a catalyst a small amount of a previous oxidation product which has been found to be satisfactory may be added in order to reduce the normal induction period. When a temperature of at least about 210° F. and preferably 230° F. is reached, air or a gas containing free oxygen is blown into the wax. During the air blowing the pressure is maintained between normal atmospheric pressure and about 500 pounds gage and preferably between about 80 and about 150 pounds gage. The air blowing rate, which is extremely critical, is maintained between about 0.25 and about 1.2 standard cubic feet per minute per 100 pounds of paraffin wax at the start of the oxidation and the rate of blowing is gradually increased as the oxidation proceeds until it reaches a value between about 1.5 and about 5.0 standard cubic feet per minute per 100 pounds of charge after passing an induction period. This latter rate is maintained until the oxygen utilization becomes low as determined by oxygen analysis of the off-gas. At this stage the rate of blowing is again decreased and maintained at such a rate that the oxygen content of the off-gas is less than 5 to 10%. The time required to effect the desired oxidation is found to vary but will generally be between about 50 and about 150 to 200 hours.

It is extremely essential that the air entering the wax be dispersed in fine bubbles so that good contact of air and wax is obtained. This is suitably realized by blow-

ing the air through a porous ceramic, glass, Alundum or stainless steel plate or disc positioned near the bottom of the oxidation vessel. Sintered stainless steel plates or diffusion discs and porous Alundum discs having pore sizes of between approximately 5 and 10 microns have been found to give exceptionally good results. During the oxidation, volatile materials carried out of the oxidation vessel with the spent air or other gas used for oxidation are preferably returned to the oxidation unit by refluxing. These volatile materials comprise mainly water and formic acid together with other partial oxidation products, as for example, lower molecular weight alcohols, ketones, esters and the like. Thus, the oxidation is preferably effected with refluxing or partial refluxing of volatile products back to the oxidation unit. It is believed that the oxidation proceeds through the formation of transient intermediate peroxides, as for example, through performic acid. Under the conditions of the oxidation the life of these intermediates is very short. However, it is observed that the presence of at least minor amounts of the reflux stream has the effect of increasing the rate and regulating the course of the oxidation. Formic acid is not the only source of reactive intermediates, however, as oxidation runs have been made with the addition of pure aqueous formic acid solutions which did not proceed at as rapid rates as the runs made with the return of reflux to the oxidizer.

The air-blowing rate indicated hereinabove is extremely important. Thus, it is found that if the air rate is too great, i.e., is greater than the limits specified particularly during the initial part of the oxidation, the oxidation does not proceed in the manner desired. With higher initial air rates it is possible to obtain an acid number of 300 to 400 mg. KOH/g., but when the acid number reaches about this value further increase in acid number does not take place. Continued air blowing results in resinification and darkening of the oxidized product. Moreover, the temperature at which oxidation is effected must be maintained within the limits indicated. Thus, if oxidation is effected at temperatures below about 210° F., the acid number of the oxidized product, when acid number increase ceases or becomes negligible, is not in the desired range. Generally, it is impossible to obtain acid numbers higher than about 300 to 400 mg. KOH/g. under such circumstances. Moreover, if during the period of oxidation the temperature of the wax being oxidized is permitted to rise above about 260° F. it is found to be impossible to obtain a product having the desired high acid number. Resinification and darkening are rapid at the higher temperatures.

The time of oxidation is dependent upon conditions under which oxidation is effected and the time will vary depending upon how closely the critical conditions of oxidation are complied with. Although, as indicated above, the time usually varies between 50 and about 200 hours, generally if the conditions of oxidation are maintained in the optimum ranges, the oxidation will be complete in about 60 to about 100 hours. Although in certain instances products having acid numbers as high as 500 to 550 have been obtained using an oxidation time of as high as 200 to 250 hours, generally the character of the oxidation product is somewhat inferior when such long periods of oxidation are required in order to obtain the desired high acid number. The long heating periods appear to promote resinification.

Catalysts which may be employed and which serve to initiate the oxidation reaction include metal salts or soaps such as manganese naphthenate, manganese oleate, cobalt naphthenate, cobalt oleate and the corresponding lead soaps. Alkaline permanganate or alkaline manganese dioxide are also excellent catalysts. Manganese naphthenate has been found to be eminently satisfactory as a catalyst for these operations. It is to be pointed out that catalysts of these types are not essential since the wax may be oxidized without the use of catalyst.

However, in such cases the oxidation reaction is slow to start unless it is initiated by other means such as small amounts of the product of a prior oxidation. The induction period, during which little or no acid number increase is observed and during which little or no oxygen is absorbed, can be greatly decreased by the use of other added catalysts. This induction period, even in the presence of manganese soap, may be as long as 16–36 hours. The addition of small amounts, i.e., 0.1% to 1%, of a hydrocarbon peroxide such as di-lauryl peroxide decreases the induction period to 1–3 hours. A completely satisfactory replacement of such peroxide is "pre-induced" wax. This is made simply by air blowing wax at 200–250° F. with a minimum flow of air to maintain oxygen saturation for 16–72 hours or until the induction period is passed. This operation can be carried out at atmospheric pressure, without catalysts in a mild steel vessel as the length of the induction period does not appear to be affected by these variables. "Pre-induced" wax is characterized by a peroxide number of 50–500 milli-equivalents per kilogram and an acid number of 2 to 20 mg. KOH/g. The product is a material superficially resembling wax and can be stored without decomposition for several months. Amounts of pre-induced wax to be used will be between 0.1% to 1 or 2%.

This pre-induced wax is not to be confused with oxidized wax which is oxidized under conditions which prevent the attainment of high acid number products. Thus, it is noted that small amounts of oxidized wax obtained by a process which results in final products in which the acid number cannot be made as high as about 490–500 mg. KOH/g. appear to prevent the desired oxidation in subsequent batches. For this reason, if a given oxidation run results in a product which reaches a maximum acid number of less than about 490 mg. KOH/g. it is essential that the oxidation vessel be completely cleaned before attempting to produce oxidized waxes having the characteristics desired. This can be done by washing the vessel with hot acetone, then with aqueous sodium hydroxide, followed by water washing until neutral. A second wash with acetone to dry the vessel is desirable. Other equivalent means may of course be used. Dilute nitric acid washes are especially valuable in cases of extreme inactivation.

When samples of the oxidized product removed at intervals from the oxidation vessel indicate that the oxidation has proceeded to a sufficient degree, as indicated by an acid number of at least about 460 mg. KOH/g., and preferably that the oxidation has proceeded to a point where there is no further increase in acid number on continued air blowing and the acid number is at least 490 mg. (KOH/g.), the product is considered satisfactory. A typical oxidized wax will have an acid number of about 520 mg. KOH/g., a saponification number of about 650 mg. KOH/g., and will be a light amber color. This typical oxidized wax will have a saponification number-acid number ratio of 1.25. This ratio, which indicates the proportion of esters or ester-like materials present in the oxidation product, has been found to vary from about 1.2 to 1.32 to 1 and generally will be in the range of 1.22 to 1.3 to 1. It is to be noted in this connection that oxidation products obtained from paraffin wax where the maximum acid number obtainable during the oxidation is about 450 or less or which are dark brown colored will have saponification number-acid number ratios of at least about 1.50 and generally above about 1.7 to 1.

The term "acid number" as used herein represents the numerical value of the acidity and is determined by methods described in A.S.T.M. Standard on Petroleum Products and Lubricants. Acid numbers of the acidic fractions obtained by oxidation of paraffin wax are determined according to the method described in the October 1947 edition, page 639. Acid number determinations on esters produced herein are made according to the

method described on page 425 of the November 1950 edition.

The term "saponification number" as used herein is the saponification equivalent as determined by the method described in A.S.T.M. Standards on Petroleum Products and Lubricants, November 1950, page 39. Both acid number and saponification number values are expressed in milligrams of KOH per gram of sample.

Oxidized paraffin wax produced as described above prior to esterification is preferably topped to remove the lower molecular weight monocarboxylic acids and partial oxidation products together with water, at a temperature of 300° F. and a pressure of 1–2 mm. This temperature is below that at which succinic acid distills. The resulting topped, oxidized product is suitable for use without further treatment in the preparation of the esters of this invention, provided that the oxidized wax has an acid number of at least about 460.

A second method of separating a fraction of acids suitable for use in preparing the polymerized esters which method is applicable to oxidized waxes having acid numbers above about 490 mg. KOH/g. consists in extracting the oxidized paraffin wax with water, as for example, with two equal volume portions of water at about 150–200° F. and vaporizing the water and lower boiling acids from the water extract. In such extractions, it is also feasible to use in place of water, mixtures of water and low molecular weight alcohols, as for example, methyl, ethyl and propyl alcohols, wherein water comprises at least about 50% by volume of the water-alcohol mixture. Mixtures of water and low molecular weight fatty acids are useful selective solvents for this separation. Especially desirable is a mixture of formic acid and water recovered from the wax oxidation step. By adjustment of distillation conditions, aqueous formic acid solutions of nearly any desired concentration may be obtained. The atmospheric pressure aqueous azeotrope, containing 77.5% formic acid is a preferred solvent.

Still another method of separating a fraction of dicarboxylic acids suitable for use in preparing the esters, which method is applicable to waxes having acid numbers above about 460, is to extract the oxidized wax and preferably the topped, oxidized wax with a light petroleum hydrocarbon, as for example, pentane, hexane or mixtures of low boiling hydrocarbons comprising pentane and/or hexane, thus light petroleum naphthas may be used for the extraction. The portion of the oxidized material insoluble in naphtha or other hydrocarbon is the fraction to be used in the preparation of the esters.

It is to be noted that each of the methods described above is designed to eliminate from the oxidized wax the monocarboxylic acids and the non-acidic materials.

The polymerized glycol and polyglycol esters of the mixture of dicarboxylic acids may be made by direct esterification but are preferably prepared by first converting the mixtures of dicarboxylic acids produced as described hereinabove into simple esters using a low molecular weight aliphatic alcohol having less than about 9 carbon atoms and preferably less than about 7 carbon atoms per molecule. Thus, the acids may first be esterified using methyl, ethyl, propyl, butyl, amyl or other lower molecular weight alcohol, up to and including the octyl alcohols. The simple esters are then purified as by distillation and converted into the desired glycol or polyglycol esters by ester exchange with the desired glycol or polyglycol. Polymerization of the glycol or polyglycol esters occurs during the heat treatment necessary to effect completion of the ester exchange reaction and removal of the monohydric alcohol and excess glycol or polyglycol from the resulting ester.

The initial esterification with the monohydric alcohol is effected using well known conditions for esterification. The mixture of acids is heated with the alcohol, as for example, n-butanol, in the presence of an acid

catalyst, such as phosphoric acid, sulfuric acid, hydrogen chloride, benzene, toluene, or lower alkyl sulfonic acids, stannous chloride, zinc chloride or the like. The amount of catalyst to be employed will generally be in the range of between 0.05 to 2.0% by weight, based on the esterification charge. An excess of alcohol is employed, as for example, 10 to 100% excess over that theoretically required to esterify all of the acid groups of the dibasic acids in order to insure complete esterification of the acids. Additional water entraining agents such as petroleum naphthas, benzene, toluene or xylene may also be added. The esterification is effected under reflux at temperatures of 120 to 390° F., depending upon the alcohol employed. When n-butanol is employed, temperatures of refluxing are approximately 230 to 360° F. During the refluxing, water is removed from the reflux line by means of a water trap. When the esterification reaction is substantially complete, as indicated by the fact that no further water is formed and by the fact that the acid number of the reaction mixture reaches a low, constant value, the resulting esterified product is vacuum distilled to remove a first overhead fraction comprising excess alcohol and lower molecular weight fatty acid esters, if such are present. The distillation is continued at pressures of 0.5–2 mm. to a pot temperature within the range of about 435° F. to 480° F. until incipient cracking is observed in the distillation bottoms to recover as a second overhead fraction a pale yellowish product consisting of monohydroxy alcohol esters of the mixture of dicarboxylic acids. The yield of esters in this process generally amounts to 90–120% by weight of the acids charged to the esterification reaction. It is often advantageous to neutralize the excess acidity of the ester mixture before distillation to minimize thermal decomposition. This may be done by a dilute alkaline wash, by treatment with an anion exchange resin or by carrying out the distillation in the presence of slightly over the stoichiometric quantity of a mild alkali, such as sodium carbonate or acetate, calcium or magnesium carbonate or acetate.

The esters produced as above described are converted into polymerized glycol or polyglycol esters by reaction with a glycol or polyglycol in the presence of between 0.05% and 1.0% by weight based on the charge of an ester exchange catalyst, as for example, stannous chloride.

The presence of a catalyst is essential to the reaction, as carefully purified n-butyl esters have been found to not undergo the ester exchange reaction with glycol under the conditions shown in the absence of catalysts. Higher temperatures are required with resultant darkening of the ester or sometimes simply in removal of the glycol by distillation. Many catalysts are effective for the exchange reaction although stannous chloride is preferred as it appears to impart some degree of heat and oxidation stability to the resulting polyester. Such catalysts as sodium carbonate, sodium acetate, sodium, potassium, calcium or lead soaps, litharge, zinc chloride, zinc borate, cadmium salts and soaps, etc., are all active catalysts. The ester exchange reaction is effected by heating one equivalent of the simple ester with between about 1.5 to 2.5 equivalents of glycol or polyglycol at temperatures of 320° F. to 500° F. with inert gas stripping using a catalyst. During this heat treatment the monohydric alcohol produced in the ester exchange reaction is vaporized and removed from the system. The inert gas to be employed, is preferably carbon dioxide or nitrogen although other inert gases, including methane, ethane, fuel gas and the like, may be used for the stripping operation. Heating is continued until no further distillate is obtained. This reaction is generally complete in from 1 to 5 hours.

Following the completion of the above ester exchange reaction as indicated by the complete removal of monohydroxy alcohol, the product is vacuum topped, prefer-

ably with inert gas stripping, to remove low molecular weight materials including the excess glycol or polyglycol present in the reaction mixture. This topping is continued until no further distillation is obtained at a pot temperature of 445–465° F. at about 0.5 mm. pressure. The distillation bottoms material consists of polymerized glycol or polyglycol esters. It has a light yellow to light brownish color and is a viscous liquid having a molecular weight between about 700 and about 4000. Molecular weight determinations have been made using the ebullioscopic method in benzene solution. This ester material will have a viscosity ranging from about 100 to about 100,000 centistokes at 110° F. and from about 50 to about 50,000 centistokes at 210° F. The products formed from the glycol components listed below are found to be completely miscible with ester type synthetic lubricating oils at all temperatures.

The glycols and polyglycols which may be employed in preparing the polymerized esters of this invention include glycols having at least 4 carbon atoms per molecule and polyglycols in which each glycol unit contains at least 3 carbon atoms. Thus the butylene and higher molecular weight glycols and the polypropylene and higher polyglycols may be employed. Polyester products obtained with the lower glycols, i.e., ethylene and propylene glycols; and polyglycols, i.e., the di, tri, etc. ethylene glycols, are not sufficiently soluble in ester type synthetic oils to be useful.

The useful glycols include butanediol-1,3, butanediol-1,4, pentanediol-1,5, hexanediol-1,6, and like diols which may be normal or branched chain compounds. Thus, compounds such as 2,2-dimethylpropanediol-1,3, 2,2-diethylpropanediol-1,3, 2-ethyl-2-butylpropanediol-1,3, 2-ethylhexanediol-1,3, and similar branched chain glycols are useful.

The hydroxyl groups may be primary or secondary, however, those diols in which the hydroxyl groups are primary are preferred. Tertiary hydroxyl groups are removed by dehydration under the conditions of the ester exchange. Although the glycols must have at least 4 carbon atoms, the upper limit of carbon atom content does not appear to be critical. Glycols having as high as 12 carbon atoms or even as high as 18 carbon atoms per molecule appear to have utility. Thus dodecanediol-1,12, and octadecanediol-1,12 are found to produce polyesters having the desired properties. In addition to the simple glycols those having alkoxy substituents may be employed. Thus, 2-ethoxymethyl-2,4-dimethylpentanediol-1,5 and similar ethoxy and methoxy derivatives of glycols have utility.

The preferred polyglycols include the di, tri and higher polypropylene glycols and the di-tri and higher polybutylene glycols, however, any of the polyglycols corresponding to the useful glycols listed hereabove may be employed in forming the polyesters described herein.

In adding the polymerized glycol or polyglycol esters to ester type synthetic lubricating oils to produce lubricants having the desired extreme pressure and/or anti-seize characteristics generally between about 2% and about 15% by weight of the polyesters will be employed. The effect of these percentages of polyesters in imparting the desirable characteristics to synthetic lubricating oils has been determined using the Shell 4-ball tester. This is a well known apparatus used in the industry for evaluating lubricants so that more than a brief description of the machine and test method is not believed to be necessary. In brief, a pyramid of four hardened steel balls is placed in a machine which holds three of the balls stationary and rotates the top ball in contact with the stationary balls under given pressures. The balls are lubricated with the oil being tested and the top ball which is loaded by a lever and weight device is rotated at a rate of approximately 1735 r.p.m. for a given time or until seizure or welding occurs. In this test synthetic lubricants of the ester type permit seizure and welding of the

balls immediately or after approximately 1 to 10 seconds at loads of 120 kilograms. Such synthetic lubricating oils containing between 2 and 15% by weight of the polyesters of this invention have been found to prevent seizure, scuffing or welding for periods of at least 1 minute under loads of 120 kilograms. This test is a requirement of Military Specification Mil-L-7808-A Lubricating Oil, Gas Turbine, Aircraft as a measurement of load carrying ability. The Shell 4-ball test can be run in several ways and the results calculated in several ways. However, for the purposes of this military specification, the test is run only on loads of 70 kilograms, at which load immediate seizure must not occur, and at 120 kilograms, at which load welding must not occur. For this reason, data presented herein were generally obtained at these test loads.

It has been indicated hereinbefore that the polymerized esters of this invention will have a molecular weight between about 1000 and about 4000. It is to be pointed out that by varying the heating time and temperature with some glycols and polyglycols it has been possible to prepare polymerized esters having molecular weights as low as about 700 and as high as about 5000 and these esters have performed the functions of improving extreme pressure characteristics, increasing viscosity index and reducing the pour point of synthetic ester type lubricating oils. Generally, however, it is to be noted that polymerized esters having molecular weights outside of this range fail to impart one or more of the mentioned characteristics and are therefore not the equivalent of those polyesters having a molecular weight within the mentioned range. The preferred molecular weight range for the polymerized esters is between about 1000 and about 3000 since esters falling within this range appear to be most effective in producing synthetic lubricating oils having the desired characteristics.

Synthetic lubricating oils to which the polymerized esters of this invention may be added to produce oils having the exceptional extreme pressure characteristics described herein include the ester type synthetic lubricating oils, such as those available on the market including diisooctyl adipate and di-2-ethylhexyl sebacate, as well as esters produced by reacting aliphatic monohydroxy primary alcohols, preferably those which are branched chain and have about 5 to about 14 carbon atoms per molecule, with the oxidized paraffin wax or with topped, oxidized paraffin wax as described herein. Other esters suitable for use as synthetic ester lubricants to which the polyesters of this invention may be added to produce E.P. lubricating oils include the esters obtained by reacting glycol and/or polyglycol monoalkyl ethers with oxidized paraffin wax or topped, oxidized paraffin wax as described herein.

The aliphatic alcohols which are useful will thus include the various amyl, hexyl, heptyl, octyl, nonyl etc. alcohols, up to those alcohols containing approximately 14 carbon atoms per molecule. It is observed that 2-ethyl hexanol produces particularly satisfactory synthetic lubricants as do 3,7-dimethyl octanol, 2-methyl pentanol and isoamyl alcohol.

The glycol ethers which may be employed as mentioned above include the glycol and/or polyglycol monoalkyl ethers in which the alkyl group of the ether is a radical having between about 3 and about 12 carbon atoms per molecule and preferably between about 3 and about 9 carbon atoms per molecule. The alkyl radical may be straight or branched chain and may therefore be a normal or branched chain propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl radical. Also, mixtures of these radicals may be present in the ethers. The glycol or polyglycol group of the glycol monoalkyl ethers which have utility in preparing the synthetic ester lubricants include ethylene glycol, propylene glycol, butylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, diethylene glycol, tri-

ethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol and tributylene glycol.

Thus compounds which may be used to form the ester lubricants by esterification with the mixed dicarboxylic acids obtained by oxidizing paraffin wax include ethylene glycol mono-(2-ethylbutyl) ether, ethylene glycol mono-(2-ethylhexyl) ether, ethylene glycol mono-(1-methylheptyl) ether, propylene glycol mono-n-amyl ether, propylene glycol mono-(2-ethylbutyl) ether, butylene glycol mono-isopropyl ether, butylene glycol mono-n-butyl ether, trimethylene glycol mono-2-ethylhexyl ether, tetramethylene glycol mono-n-propyl ether, pentamethylene glycol mono-isobutyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-(1-methylbutyl) ether, diethylene glycol mono-(2-ethylhexyl) ether, diethylene glycol mono-(3-methylbutyl) ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-n-butyl ether, dibutylene glycol mono-n-hexyl ether, dibutylene glycol mono-(2-ethylhexyl) ether, triethylene glycol mono-n-butyl ether, triethylene glycol mono-isobutyl ether, triethylene glycol mono-n-propyl ether, tripropylene glycol mono-n-propyl ether, tripropylene glycol mono-n-butyl ether, tripropylene glycol mono-(2-ethylbutyl) ether, tributylene glycol mono-(2-ethylbutyl) ether, tributylene glycol mono-n-butyl ether and tributylene glycol mono-isopropyl ether.

The preferred ethers include ethylene glycol mono-(2-ethylbutyl) ether and the corresponding 2-ethylhexyl ether, dipropylene glycol mono-n-propyl ether and the corresponding n-butyl ether and tripropylene glycol mono-n-propyl ether and the corresponding n-butyl ether.

The ester lubricants prepared with either the monohydroxy alcohol or the described glycol or polyglycol ethers are preferably prepared directly from the crude oxidized wax or topped oxidized wax by reaction with the desired alcohol or ether, preferably about 1 equivalent of acid based on the acid number will be reacted with between about 1.1 and 1.5 equivalents of alcohol. The crude oxidate or fraction thereof is placed in a vessel fitted with a reflux condenser having a water trap in the reflux line and the desired alcohol is added along with 0.5 to about 2 volumes of naphtha, toluene or the like, which serves as a solvent and as a carrying agent or azeotroping agent for water produced during the esterification reaction. The mixture is heated and refluxed until the acid number of the product is 15 mg. KOH/g., or lower. In some instances it is possible to obtain acid numbers as low as 2 to 3 mg. KOH/g. without using unreasonably long esterification times. The esterification is considered complete when no further quantities of water are obtained in the water trap. During the esterification about 0.1% to about 1% by weight of a catalyst is employed. Catalysts which have been found to have utility in this process include the zinc, aluminum, cadmium, and tin chlorides, sulfuric acid, toluene sulfonic acid and the like. The salt-type catalysts, and particularly stannous chloride are the preferred catalytic agents. However, ethane and toluene sulfonic acids are particularly active in aiding the esterification reaction.

Following completion of the esterification reaction the product may be topped to remove solvent, i.e., naphtha or toluene or the like and may be further purified, if desired, particularly where special characteristics are desired. Thus, the product may be treated with dilute caustic, carbonate or bicarbonate solutions such as sodium carbonate or bicarbonate to extract the remaining acidic bodies. The material may be treated with clay, activated charcoal or other adsorbent treating agents to remove colored bodies and the like.

Removal of acid and color bodies is most readily effected by contacting the ester or preferably a naphtha or toluene solution of the ester with a porous weak-base anion exchange resin. Such resins are commercially available. Two that have been used with success are "Permutit DR," obtainable from Permutit Corporation, 330

West Forty Second Street, New York, and "Duolite S-30," obtainable from Chemical Process Company, 901 Spring Street, Redwood City, California. Samples of esters which have been contacted with such resins have been found to have acid numbers of substantially zero and have a very light amber color. In this method of treatment any of the porous weak-base anion exchange resins available on the market appear to be suitable. Since the available resins are generally designed for use in aqueous systems and are available as water wet materials they must be converted for the present use by activating the resin with aqueous sodium hydroxide solution containing approximately 5% sodium hydroxide or with an isopropanol solution of ammonia. When the resin is activated by treatment with sodium hydroxide it is preferably rinsed with distilled water until the pH of the effluent liquid is reduced to 8 or 9 and subsequently rinsed with about 2 bed volumes of a water miscible solvent such as a ketone or alcohol to remove water from the resin. Isopropanol is particularly satisfactory for this purpose. The resin is then rinsed with a low boiling naphtha to remove the water miscible solvent and is ready for use. Resins so prepared are found to selectively absorb the color bodies and acidic bodies from the esters and result in a reduction in acid number and in color improvement of the ester products. These resins are regenerated for use by treatment with aqueous sodium hydroxide as above described or they may be regenerated by treatment with alcoholic ammonia followed by washing with a low boiling naphtha.

The esters produced as described hereinabove will have pour points of -30°F. to -100°F. and generally will have pour points between -50°F. and -100°F. The viscosities will vary between about 3 and 35 centistokes at 100°F. and will generally be between 5 and 20 centistokes at 100°F. The viscosity indices of these oils will usually be between about 95 and 150. Typical esters will have flash points between about 300°F. and about 500°F. The esters are miscible in all proportions with mineral oil fractions, particularly those in the light lubricating oil ranges as well as with other synthetic lubricating oils.

The following examples illustrate various features of this invention.

Example I

A mixture of dicarboxylic acids suitable for use in preparing the glycol and polyglycol esters of this invention and for preparing the synthetic ester type lubricating oils, to which the glycol and polyglycol esters may be added to produce a synthetic lubricant having exceptional antiseize characteristics as well as improved viscosity index, is prepared by oxidizing refined paraffin wax in the following manner.

Approximately 14,000 grams of a refined paraffin wax having a melting point of about 145°F. , 310 grams of pre-inducted paraffin wax as described hereinabove and 80 grams of manganous naphthenate were charged to a stainless steel oxidation vessel provided with heating and cooling coils and with means for introducing and dispersing air at a point near the bottom of the vessel. Air dispersion was obtained by using a sintered stainless steel disc having a pore size of approximately 10 microns. The wax was heated to a temperature of about 250°F. and the vessel pressured to about 130 pounds gage and air was introduced into the oxidation vessel at a rate of about 0.50 standard cubic feet per minute per 100 pounds of wax. Air blowing was continued under these conditions until analysis of the off gases indicated appreciable utilization of oxygen, i.e., until the oxygen content of the off gases dropped to approximately 2-3% of oxygen. At this time the air blowing rate was increased to 1.4 standard cubic feet per minute per 100 pounds of gage. At this point the oxidation charge had an acid number of about 20 mg. KOH/g.

As the oxidation proceeded the amount of air blown through the charge was increased and from approximately the 21st hour to the 75th hour of oxidation the air rate varied from about 2.5 to 4.2 standard cubic feet of air per minute per 100 pounds of charge, the rate being controlled so that the off gases did not contain more than 5 to 10% of oxygen. The total time required to complete the oxidation was 95 hours and during the last 20 hours the air rate was decreased to approximately 1.2 standard cubic feet per minute per 100 pounds of charge. The resulting oxidized product had an acid number 586 mg. KOH/g.

During the oxidation, a reflux condenser was employed and approximately one-half of the normally liquid material leaving the unit with the off gases was condensed and returned to the oxidizer. The product, which amounted to 16,150 grams, had a light amber color.

Example II

A second batch of 14,000 grams of paraffin wax of the type employed in Example I was oxidized under substantially the same conditions described in that example for a total of 95 hours. In this instance the product was a light amber color and had an acid number of 598 mg. KOH/g.

This product was topped to a temperature of 345°F. at 5 mm. pressure and the resulting product had an acid number of 482 mg. KOH/g.

Example III

A synthetic lubricating oil suitable for use with the polymerized glycol and/or polyglycol esters of this invention to form lubricants having extreme pressure characteristics was prepared by refluxing a mixture of 4050 grams of the product of Example I, 6600 grams of 2-ethyl hexanol, 50 grams stannous chloride dihydrate and 4000 ml. of a paraffinic naphtha boiling between about 200°F. and 300°F. Heating and refluxing was continued for 27 hours, at which time a total of about 850 ml. of water was recovered from a water trap in the reflux line. The product was purified by percolation through a decolorizing resin column which had been activated by sodium hydroxide. The resin was a porous weak-base anion exchange resin of a commercially available type. The effluent from the resin column was stripped free of solvent, distilled under a vacuum at 2 mm. pressure to a temperature of 320°F. and the stripped product was filtered through diatomaceous earth for clarification. The product amounted to about 6050 grams and had an acid number of 0.35 mg. KOH/g., a Gardner color of 5, a pour point of -95°F. , a viscosity of 10.2 centistokes at 100°F. and a viscosity index of 103.

Example IV

An ester of the acid mixture obtained as the oxidation product in Example I was prepared using 3,7-dimethyloctanol. The alcohol was prepared from commercially pure citronellal by hydrogenation over Rufert nickel catalyst at 167°F. under an initial hydrogen pressure of 1890 pounds per square inch gage. The catalyst was removed by filtration and the resulting alcohol recovered by vacuum distillation. A selected cut boiling between 237.2°F. and 240.8°F. at 20 mm. pressure was used for esterification.

A mixture of 173 grams of the product of Example I having an acid number of 586 mg. KOH/g., 347 grams (25% excess) of 3,7-dimethyloctanol, 2 grams of stannous chloride dihydrate and 400 ml. of a paraffinic naphtha boiling between about 200°F. and about 300°F. was heated under a reflux condenser for a total of 11.5 hours. The temperature ranged from about 217°F. to about 302°F. during this treatment. A total of 41.5 ml. of water was recovered from a water trap in the reflux line. The solvent-free crude reaction product which had an acid number of 5.1 mg. KOH/g. was diluted with two

volumes of a low boiling paraffinic naphtha and percolated through a decolorizing resin column which had been activated by sodium hydroxide. The effluent from the resin column was stripped free of solvent, distilled under a vacuum of 2 mm. of mercury to a bottoms temperature of 320° F., and this stripped material was then filtered through diatomaceous earth for clarification. A light brown ester oil was obtained in a yield of 300 grams. This product had a pour point of -85° F., a kinematic viscosity of 17.6 centistokes at 100° F., an acid number of 2.8 mg. KOH/g., and a Gardner color of 10. This purified ester has properties making it particularly suitable as a synthetic lubricating oil and when polymerized glycol or polyglycol esters of this invention are added in the amounts indicated herein to this ester oil the resulting product has exceptional extreme pressure characteristics.

Example V

An ester, suitable for use in preparing an extreme pressure synthetic oil by incorporating therein polymerized glycol or polyglycol esters of this invention, was prepared by reacting 85 grams of oxidized paraffin wax produced in Example I with 207 grams of dipropylene glycol monon-butyl ether and 2 grams of stannous chloride dihydrate. The mixture was refluxed in the presence of 200 ml. of a paraffinic naphtha for 13 hours at a temperature of 265° F. to 330° F. The resulting crude ester was purified in the manner described in Example III and the purified ester had an acid number of 1.1 mg. KOH/g., a Gardner color of 11, a pour point of -78° F., a kinematic viscosity at 100° F. of 15.6 centistokes and a viscosity index of 135.

Example VI

A polymerized pentanediol-1,5 ester of the topped, oxidized wax produced in Example II was prepared by ester exchange from the n-butyl ester of the oxidized wax.

A mixture of 456 grams of topped wax oxidate from Example II, 583 grams of n-butanol and 3.5 grams of p-toluene sulfonic acid was refluxed through a water trap for 8.5 hours. At this time evolution of water had ceased and the excess butanol was removed by distillation. The resulting ester product was vacuum distilled and the material boiling between 220° F. and 440° F. (head temperature) at 2.2 mm. mercury pressure, was recovered as a very pale yellow oil. The yield was 519 grams.

A mixture of 70 grams of the distilled n-butyl ester product, 104 grams of pentanediol-1,5 and 0.7 gram of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was heated and a stream of carbon dioxide was passed through the mixture during the heating. Normal butanol distilled from the reaction mixture starting at a pot temperature of about 355° F. and removal of the n-butanol was substantially complete after about 2 hours, during which time the temperature had increased to about 410° F. The temperature was maintained between about 440° F. and 465° F. for an additional hour and the mixture was then vacuum distilled to a pot temperature of about 480° F. under 1.1 mm. mercury pressure. A yield of 63 grams of a clear, light brown viscous oil was obtained. It was readily soluble in the wax oxidate ester oils produced in Examples III, IV and V and in commercially available diester lubricating oils. This product had an acid number of 3.3 mg. KOH/g., a saponification number of 438 mg. KOH/g., and a molecular weight of 1805.

Extreme pressure synthetic lubricating oil was prepared by dissolving 10% by weight of the above polyester in the ester oil prepared as in Example III. The resulting oil had a pour point of -6° F., a kinematic viscosity in centistokes of 21.57 at 100° F. and 4.81 at 210° F. and a kinematic viscosity index of 159. This oil supported loads of 70 kilograms and 120 kilograms for 1 minute on the Shell 4-ball test without seizure.

A second extreme pressure lubricating oil was prepared

using 10% by weight of the above polyester in a commercial synthetic lubricating oil consisting of diisooctyl adipate. The resulting oil supported loads of 70 kilograms and 120 kilograms, respectively, in the Shell 4-ball test without seizure. For comparison, the product of Example III and the diisooctyl adipate without additives supported 70 pounds in the Shell 4-ball test but gave immediate seizure at 120 pounds.

Example VII

A polymerized dipropylene glycol ester of the topped wax oxidate produced in Example II was prepared by first converting the wax fraction to the n-butyl ester as described in the first paragraph of Example VI and then converting the n-butyl ester to the polydipropylene glycol ester by ester exchange under substantially the same conditions as set forth in Example VI.

Following removal of the n-butanol released in the ester exchange reaction, the mixture was heated for an additional hour at temperatures between 440° F. and 465° F. to complete the reaction and effect polymerization. The resulting product was vacuum distilled to a pot temperature of 480° F. at 1.1 mm. mercury pressure. This product was a clear, light brown viscous oil which was readily soluble in the esters produced in Examples III, IV and VI, as well as in commercially available diester lubricants. It had an acid number of 2.7 mg. KOH/g., a saponification number of 413 mg. KOH/g. and a molecular weight of 2600.

A lubricating oil was prepared by dissolving 10% of the above produced polyester in the product of Example III and this oil had a pour point of -90° F., a kinematic viscosity in centistokes of 18.45 at 100° F. and 4.18 at 210° F. and a kinematic viscosity index of 154. This oil supported loads of 70 kilograms and 120 kilograms in the Shell 4-ball test without seizure.

A second oil prepared by dissolving 10% by weight of the above polyester in diisooctyl adipate supported 70 kilograms and 120 kilograms in the Shell 4-ball test without seizure, whereas, the product of Example III, as well as the diisooctyl adipate both permitted seizure at 120 kilogram load in the tests.

A third oil was prepared using 15% by weight of the polymerized ester in the product of Example III. The resulting oil supported 120 kilograms in the Shell 4-ball test and in physical properties was similar to the corresponding oil containing 10% of the polymerized ester.

A fourth oil was prepared using 2% by weight of the polymerized ester in the product of Example III. This oil had improved viscosity index and showed better extreme pressure characteristics than the base oil.

A fifth oil prepared with the product of Example IV by dissolving 5% by weight of the polymerized ester had similar properties to the first oil described in this example.

Example VIII

Example VI was repeated using an equivalent quantity of 2-ethoxymethyl-2,4-dimethyl pentanediol-1,5 in place of pentamethylene glycol. The resulting distilled product was a light yellow, soluble oil having an acid number of 1.7 mg. KOH/g., a saponification number of 323 mg. KOH/g., and a molecular weight of 1765.

A synthetic lubricating oil having extreme pressure characteristics was prepared by dissolving 10% by weight of the above produced polyester in the product of Example III. The resulting oil had a pour point of -86° F., a kinematic viscosity in centistokes of 17.42 at 100° F. and 3.90 at 210° F., and a kinematic viscosity index of 138. The resulting oil supported loads of 70 kilograms and 120 kilograms in the Shell 4-ball test without seizure.

A second lubricating oil, having extreme pressure characteristics, was prepared by dissolving 10% by weight of the above polyester in the product of Example V. The resulting oil supported loads of 70 kilograms and 120

kilograms in the Shell 4-ball test without seizure, whereas, the product of Example V gave immediate seizure in the test at a load of 120 kilograms.

Example IX

A polyester was prepared following the procedure outlined in Example VI, using 2-ethylhexanediol-1,3. The resulting polyester had a pale yellow color and was readily soluble in ester oils. The product had an acid number of 0.75 mg. KOH/g., a saponification number of 3.72 mg. KOH/g. and a molecular weight of 1110.

An extreme pressure lubricating oil was prepared by dissolving 10% by weight of the above polyester in the product of Example III. This oil had a pour point of -78° , a kinematic viscosity in centistokes of 15.40 at 100° F. and 3.51 at 210° F. and a kinematic viscosity index of 122. This oil supported loads of 70 kilograms and 120 kilograms, respectively, without seizure in the Shell 4-ball test.

Example X

To show the importance of adding glycols of low carbon atom content and ethylene glycol or triethylene glycol, esters of the product of Example II were prepared with each of these mentioned glycols. In neither case was the product sufficiently soluble in synthetic oils to be of value as an extreme pressure additive.

The foregoing description and examples are illustrative of the invention but are not to be taken as limiting the invention since many variations may be made without departing from the spirit and the scope of the following claims.

I claim:

1. A composition adapted for addition to ester lubricating oils, which ester lubricating oils are selected from the class consisting of monohydroxy aliphatic alcohol diesters of dicarboxylic acids, glycol monoalkyl ether esters of dicarboxylic acids, and polyglycol monoalkyl ether esters of dicarboxylic acids, to impart extreme pressure characteristics to said oils, said composition consisting essentially of a completely esterified, polymerized glycol ester of a mixture of dicarboxylic acids obtained by oxidizing refined paraffin wax which is relatively oil-free and free from asphaltic and resinous materials, and which has a melting point between about 120° F. and about 165° F. with a gas containing free oxygen in the liquid phase at temperatures between about 210° F. and about 260° F. until the acid number of the product is between about 460 and about 600 mg. KOH/g. and separating from the oxidized paraffin wax a fraction comprising dicarboxylic acids, said glycol being a glycol selected from the class consisting of glycols containing at least 4 carbon atoms per molecule and polyglycols containing at least 3 carbon atoms per glycol unit.

2. A composition adapted for addition to ester lubricating oils, which ester lubricating oils are selected from the class consisting of monohydroxy aliphatic alcohol diesters of dicarboxylic acids, glycol monoalkyl ether esters of dicarboxylic acids, and polyglycol monoalkyl ether esters of dicarboxylic acids, to impart extreme pressure characteristics to said oils, said composition consisting essentially of a completely esterified, polymerized ester of a mixture of dicarboxylic acids and a glycol selected from the class consisting of glycols containing at least 4 carbon atoms per molecule and polyglycols containing at least 3 carbon atoms per glycol unit, said mixture of dicarboxylic acids being obtained by oxidizing refined paraffin wax which is relatively oil-free and free from asphaltic and resinous materials, and which has a melting point between about 120° F. and about 165° F. with a gas containing free oxygen in the liquid phase at temperatures between about 210° F. and about 260° F. until the acid number of the product is between about 460 and about 600 mg. KOH/g. and topping the oxidized product to a temperature of about 300° F. at a pressure

of about 2 mm. of mercury to remove lower molecular weight monocarboxylic acids and partial oxidation products.

3. A composition according to claim 2 in which said glycol is dipropylene glycol.

4. A composition according to claim 2 in which said glycol is pentanediol-1,5.

5. A composition according to claim 2 in which said glycol is 2-ethylhexanediol-1,3.

6. A composition adapted for addition to ester lubricating oils, which ester lubricating oils are selected from the class consisting of monohydroxy aliphatic alcohol diesters of dicarboxylic acids, glycol monoalkyl ether esters of dicarboxylic acids, and polyglycol monoalkyl ether esters of dicarboxylic acids, to impart extreme pressure characteristics to said oils, said composition being prepared by oxidizing refined paraffin wax which is relatively oil-free and free from asphaltic and resinous materials, and which has a melting point between about 120° F. and about 165° F. with a gas containing free oxygen in the liquid phase at temperatures between about 210° F. and about 260° F. until the acid number of the product is between about 460 and about 600 mg. KOH/g., separating a fraction comprising dicarboxylic acids from the oxidized product, completely esterifying the separated fraction with a low molecular weight aliphatic alcohol having less than 7 carbon atoms per molecule and reacting the resulting esters with a glycol selected from the class consisting of glycols containing at least 4 carbon atoms per molecule and polyglycols containing at least 3 carbon atoms per glycol unit in the presence of an ester exchange catalyst at temperatures between 320° F. and 500° F. to form the corresponding glycol esters and distilling the resulting product to a temperature sufficient to remove excess unreacted glycol, thereby forming a completely esterified, polymerized glycol ester having a molecular weight between about 700 and about 5000.

7. A composition according to claim 6 in which said fraction comprising dicarboxylic acids is separated from the oxidized paraffin wax by topping the oxidized wax to a temperature of about 300° F. at a pressure of about 2 mm. of mercury.

8. A composition according to claim 6 in which said polymerized glycol ester has a molecular weight between about 1000 and about 3000.

9. An extreme pressure lubricating oil consisting of an ester lubricating oil, which ester lubricating oil is selected from the class consisting of monohydroxy aliphatic alcohol diesters of dicarboxylic acids, glycol monoalkyl ether esters of dicarboxylic acids, and polyglycol monoalkyl ether esters of dicarboxylic acids, containing between about 2% and about 15% by weight of a completely esterified polymerized glycol ester of a mixture of dicarboxylic acids obtained by oxidizing refined paraffin wax which is relatively oil-free and free from asphaltic and resinous materials, and which has a melting point between about 120° F. and about 165° F. with a gas containing free oxygen in the liquid phase at temperatures between about 210° F. and about 260° F. until the acid number of the product is between about 460 and about 600 mg. KOH/g. and separating from the oxidized paraffin wax a fraction comprising dicarboxylic acids, said glycol being a glycol selected from the class consisting of glycols containing at least 4 carbon atoms per molecule and polyglycols containing at least 3 carbon atoms per glycol unit.

10. An extreme pressure lubricating oil consisting of an ester lubricating oil, which ester lubricating oil is selected from the class consisting of monohydroxy aliphatic alcohol diesters of dicarboxylic acids, glycol monoalkyl ether esters of dicarboxylic acids, and polyglycol monoalkyl ether esters of dicarboxylic acids, containing between about 2% and about 15% by weight of a completely esterified polymerized ester of a mixture of dicarboxylic acids and a glycol selected from the class con-

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sisting of glycols containing at least 4 carbon atoms per molecule and polyglycols containing at least 3 carbon atoms per glycol unit, said mixture of dicarboxylic acids being obtained by oxidizing refined paraffin wax which is relatively oil-free and free from asphaltic and resinous materials, and which has a melting point between about 120° F. and about 165° F. with a gas containing free oxygen in the liquid phase at temperatures between about 210° F. and about 260° F. until the acid number of the product is between about 460 and about 600 mg. KOH/g. and topping the oxidized product to a temperature of about 300° F. at a pressure of about 2 mm. of mercury to remove lower molecular weight monocarboxylic acids and partial oxidation products.

11. A lubricating oil according to claim 10 in which said glycol is dipropylene glycol.

12. A lubricating oil according to claim 10 in which said glycol is 2-ethylhexanediol-1,3.

13. An extreme pressure lubricating oil consisting of an ester lubricating oil, which ester lubricating oil is selected from the class consisting of monohydroxy aliphatic alcohol diesters of dicarboxylic acids, glycol monoalkyl ether esters of dicarboxylic acids, and polyglycol monoalkyl ether esters of dicarboxylic acids, containing between about 2% and about 15% by weight of a completely esterified polymerized ester, said ester being prepared by oxidizing refined paraffin wax which is relatively oil-free and free from asphaltic and resinous materials, and which has a melting point between about 120° F. and about 165° F. with a gas containing free oxygen in the liquid phase at temperatures between about 210° F. and about 260° F. until the acid number of the product is between about 460 and about 600 mg. KOH/g., separating a fraction comprising dicarboxylic acids from the oxidized product, esterifying the separated fraction with a low molecular weight aliphatic alcohol having less than 7 carbon atoms per molecule and reacting the resulting ester with a glycol selected from the class consisting of glycols containing at least 4 carbon atoms per molecule and polyglycols containing at least 3 carbon atoms per glycol unit in the presence of an ester exchange catalyst at temperatures between 320° F. and 500° F. to form the corresponding glycol esters and distilling the resulting product to a temperature sufficient to remove excess unreacted glycol, thereby forming a polymerized glycol ester having a molecular weight between about 700 and about 5000.

14. A lubricating oil according to claim 13 in which said polymerized glycol ester has a molecular weight between 1000 and 3000.

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15. A lubricating oil according to claim 13 in which said amount of polymerized glycol ester is about 10% by weight.

16. A method of preparing a composition suitable for addition to ester lubricating oils, which ester lubricating oils are selected from the class consisting of monohydroxy aliphatic alcohol diesters of dicarboxylic acids, glycol monoalkyl ether esters of dicarboxylic acids, and polyglycol monoalkyl ether esters of dicarboxylic acids, to impart extreme pressure characteristics to said oils which comprises oxidizing refined paraffin wax which is relatively oil-free and free from asphaltic and resinous materials, and which has a melting point between about 120° F. and about 165° F. with a gas containing free oxygen in the liquid phase at temperatures between about 210° F. and about 260° F. until the acid number of the product is between about 460 and about 600 mg. KOH/g., separating from the oxidized paraffin wax a fraction boiling above 300° F. at 1 to 2 mm. of mercury pressure comprising dicarboxylic acids, converting said fraction comprising dicarboxylic acids to completely esterified, simple alcohol esters by reaction with a low molecular weight aliphatic alcohol having less than about 7 carbon atoms per molecule in the presence of an acid catalyst, reacting the resulting simple esters with a glycol selected from the class consisting of glycols containing at least 4 carbon atoms per molecule and polyglycols containing at least 3 carbon atoms per glycol unit at temperatures between 320° F. and 500° F. in the presence of an ester exchange catalyst and topping the resulting product at a pressure of about 0.5 mm. to a temperature of about 445° F. to about 465° F. to leave as bottoms a completely esterified, polymerized ester.

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