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# ESTERS OF MIXED DICARBOXYLIC ACIDS

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This invention relates to new compositions of matter and more particularly it relates to complex esters of glycol and/or polyglycol monoalkyl ethers and mixtures of dicarboxylic acids and to methods for the production of such complex esters. It relates also to the mixtures of acids suitable for use in the preparation of such esters and to methods of producing the dicarboxylic acids from paraffin wax.

The invention relates more particularly to synthetic lubricants, both oils and greases, which lubricants comprise complex esters having extremely low pour point characteristics, high viscosity indices, and viscosities in the range making them particularly suitable for use as lubricants for aircraft engines, especially turbo-jet and turbo-jet propeller engines. The esters are suitable for use as lubricants in other utilizations where high viscosity index and low pour point properties together with good stability, oxidation resistance, lack of corrosiveness, and the like are desirable.

The invention also relates to compositions, particularly lubricating compositions, containing such mixed esters. Thus it relates to lubricants comprising mixtures of mineral lubricating oils and the complex esters and to greases comprising the complex esters thickened to grease consistency with metal soaps, complex metal soaps, or mineral thickeners.

Although oily esters suitable for use as lubricating oils have in the past been prepared from dicarboxylic acids and monohydric aliphatic alcohols, generally the products obtained are of extremely high cost making their use as lubricants highly uneconomical. In the preparation of such oils it has been the usual practice to employ a single purified dicarboxylic acid, such as for example sebacic acid, and esterify this acid with a pure alcohol as for example 2-ethyl hexyl alcohol. Because of the high cost of the alcohol and particularly the high cost of the dicarboxylic acid, the resulting ester is extremely costly to produce.

The need for lubricating oils which are superior to ordinary mineral lubricating oils for use as jet engine lubricants is apparent when it is realized that aircraft and particularly military aircraft must be capable of operation under Arctic conditions where lubricants must flow at temperatures as low as —60° F. to —75° F. or lower and must be capable of withstanding operating temperatures of the jet type engines. Thus, the lubricants employed should have pour points as low as —50° to —100° F. and be stable and relatively non-volatile at temperatures as high as 350° F. to 400° F. The kinematic viscosities in centistokes of these oils are preferably in the range of about 5 to 25 or 30 at 100° F. These characteristics are not obtainable with mineral lubricating oil fractions.

It has been found that a particular mixture of dicarboxylic acids produced by the controlled liquid phase air oxidation of paraffin wax is suitable for use in the production of mixed esters which have the desirable qualities of low pour point, high viscosity index, low volatility and good stability making them suitable for use as aircraft



engine lubricants and particularly as lubricants for turbo-jet engines and jet-propeller engines. These complex ester oils may be used without modification or they may be blended with suitable mineral lubricating oil fractions or with other ester oils, as for example 2-ethyl hexyl sebacate, or they may be converted into greases by the addition of soaps or by the use of other thickening agents as for example metal oxides, metal carbonates, powdered silica, bentonite or the like.

Although the esters of this invention used alone or used in admixture with mineral lubricating oil fractions or with other ester oils are satisfactory without modification as lubricants for most purposes, anti-rusting agents, anti-oxidation agents, extreme pressure agents, anti-wear agents and like addition agents may be added to such oils to improve their usefulness for special purposes and compositions containing one or more of these addition agents form a part of this invention.

The character of the oxidized paraffin wax to be employed in the preparation of esters suitable for use in the ester lubricants of this invention is particularly important. Thus oxidized wax products heretofore known do not form esters having the desirable characteristics. It is to be noted that although paraffin wax has been oxidized in the past at various temperatures and under various conditions of pressure, air-blowing rates, and the like, the products have consisted of monocarboxylic acids or of mixtures of mono- and dicarboxylic acids containing appreciable portions of the monocarboxylic acids. Attempts to continue the oxidation to such an extent that the proportion of dicarboxylic acids is relatively high, and that the acid number of the oxidized product is over about 350 to 400 mg. KOH/g. have not been successful. In attempting to produce high yields of dicarboxylic acid it has been found that as the oxidation proceeds the acid number gradually increases to a point in the range of 350 to 400 mg. KOH/g. and continued oxidation leads to the formation of polymerized and/or resinified bodies, to darkening of the oxidation product and to degradation of the acids already formed. Moreover, previously described processes result in the formation of oxidation products having relatively high saponification number-acid number ratios indicating the presence of relatively large proportions of esters or ester-like materials. It is apparent that esters made directly from such oxidation products contain large proportions of extraneous esters or ester-like materials which are undesirable in the ester lubricants of the present invention.

Thus, it is an object of this invention to provide complex esters of glycol and/or polyglycol monoalkyl ethers with a mixture of dicarboxylic acids obtained by the controlled liquid phase oxidation of paraffin wax and to provide a method of preparing such complex esters.

Another object of the invention is to produce complex esters having viscosity characteristics making them suitable for use as lubricants by esterifying a glycol and/or polyglycol monoalkyl ether with a mixture of dicarboxylic acids produced by the controlled liquid phase air oxidation of paraffin wax.

It is another object of the invention to prepare a synthetic lubricating oil having a high viscosity index and an extremely low pour point from relatively inexpensive ingredients.

Another object of the invention is to provide a synthetic lubricating oil comprising a complex ester of a glycol and/or polyglycol monoalkyl ether and a mixture of dicarboxylic acids obtained by the controlled liquid phase oxidation of paraffin wax, which synthetic lubricating oil is miscible with, and imparts desirable low pour point and high viscosity index characteristics, to mineral lubricating oils.

Another object of this invention is to provide a synthetic

lubricating oil suitable for use as a base oil in the preparation of lubricating oils suitable for use in aircraft engines of the turbo-jet type, which oil has good anti-oxidation, anti-rust, anti-wear and extreme pressure characteristics.

Another object of the invention is to provide a grease comprising metal soap or other thickening agent and a complex ester of a glycol and/or polyglycol monoalkyl ether and a mixture of dicarboxylic acids produced by the controlled liquid phase oxidation of paraffin wax.

A further object of this invention is to provide a method for oxidizing paraffin wax to obtain a mixture of dicarboxylic acids suitable for use in the preparation of synthetic lubricants having high viscosity indices and low pour points.

Other objects will be apparent as the description of the invention proceeds.

The above and other objects are accomplished by oxidizing refined paraffin wax in the liquid phase by contacting the wax with air or other oxygen-containing gas under specified and controlled conditions of temperature, pressure and rate of blowing with air or other oxygen-containing gas until the acid number of the oxidized product reaches at least about 490 mg. KOH/g. and preferably between about 500 and about 575 mg. KOH/g. The resulting oxidized material may be used per se or may be fractionated by one of the methods described herein and the acids of acid fractions thus obtained may be esterified with glycol and/or polyglycol monoalkyl ethers having 3 to 12 and preferably between 3 and 9 carbon atoms in the alkyl radical of the ether group. The esterification is effected at elevated temperatures using between about 1.1 and 1.5 equivalents of alcohol per equivalent of acid as determined from the acid number of the acid fraction and the esterification reaction is continued until the acid number of the resulting esterified product is below about 15 mg. KOH/g. and preferably between about 0 and 12 mg. KOH/g. The esters so produced have low pour points, high viscosity indices, relatively high flash and fire points, low volatility and viscosities in the range suitable for aircraft engine lubrication purposes.

The invention comprises the complex esters per se and compositions containing the esters. Thus improved lubricants are obtained by incorporating 10% to 75% or more of the complex esters of this invention in mineral oil fractions. Also various addition agents may be incorporated into the esters or mixtures of the esters with mineral lubricating oils to improve oxidation and stability characteristics or to improve anti-rusting characteristics of the esters or ester-mineral lubricating oil compositions and the resulting compositions form a part of this invention.

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 residua 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. Deoil 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.



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 liners 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 110 pounds gage. The air blowing rate, which is extremely critical, is maintained between about 0.75 and about 1.25 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 2.0 standard cubic feet per minute per 100 pounds of charge after 90 hours of oxidation. This latter rate is maintained from 90 hours to the end of the oxidation period. The time required to effect the desired oxidation is found to vary but will generally be between about 100 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 blowing 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 not returned to the oxidation unit. 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 without refluxing volatile products back to the oxidation unit.

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 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.

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 100 and about 200 hours, generally if the conditions of oxidation are maintained in the optimum ranges, the oxidation will be complete in about 120 to about 160 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. Manganese naphthenate has been found to be eminently satisfactory as a catalyst for these operations. It is to be pointed out that catalysts are not essential since the wax may be oxidized without the use of catalyst. However, in this case the oxidation reaction is slow to start. The oxidation reaction may be initiated by means other than the use of catalysts, for example, the product of a prior oxidation if present in small amounts serves as an oxidation initiator. It is important, however, if the oxidation is to be initiated in this manner that the prior oxdized materal to be used is one which was oxidized under the conditions set forth herein and which attained the high acid numbers described herein. Thus it has been found that if small amounts of previously oxidized paraffin wax which did not meet the specified requirements is present in the oxidizer, generally it will be impossible to effect oxidation to produce the desired high acid number of oxidized wax. Thus, if for some reason 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 unit 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.

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 490 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 of 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 developed during the oxidation is about 450 or less will have saponification number-acid number ratios of at least about 1.65 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.

As indicated hereinabove the oxidized product obtained following the teachings of this invention may be used per se in the preparation of the esters of this invention, or it may be fractionated by any one of several procedures depending upon the characteristics desired in the resulting esters. Since the product as removed from the oxidation vessel contains small amounts of formic and other low molecular acid and nonacid materials it is sometimes desirable to remove these materials by a stripping operation prior to forming derivatives. By heating to temperatures of about 225–250° F. or by blowing with inert gas or both it is possible to volatilized formic acid and nonacidic materials such as esters boiling in the same temperature range as formic acid.

Where it is desired to obtain a more nearly pure dicarboxylic acid fraction for further processing the oxidation product may be stripped to a temperature of approximately 340–345° F. at about 2 mm. presure. In this stripping operation all materials boiling below succinic acid such as low moleculer weight monocarboxylic acids and nonacid materials are eliminated.

In case it is desired to recover the higher molecular weight dicarboxylic acids from the oxidation product for separate treatment, the oxidation product may be extracted with an aromatic solvent, for example, toluene or xylene, to separate those acids which are soluble in the solvent employed. This treatment results in the rejection of succinic acid, high molecular weight polymeric acids, ester acids and the like. This same treatment may be applied to the oxidized wax product which has first been stripped to eliminate low molecular weight components, and in such case it results in the separation of a fraction of high molecular weight dicarboxylic acids relatively free from low molecular weight di- and monocarboxylic acids as well as from nonacid materials, polymeric acids, ester acids and the like.

Another means for separating particular dicarboxylic acid fractions from the oxidation product involves the exhaustive extraction of the crude oxidized wax or one of the stripped oxidized waxes with hot water to obtain a water-soluble fraction comprising relatively pure dicarboxylic acids.

Although the oxidized wax or the oxidized wax stripped and/or fractionated in one of the manners described above may be employed in the preparations of the synthetic lubricants of this invention, it is sometimes desirable to remove part or all of the solid dicarboxylic acids, particularly the succinic acid present in the oxidized product. These acids may be removed by filtering the cooled crude oxidation product or the cooled stripped oxidation product. By such treatment it has been found possible to separate a crude succinic acid amounting to approximately 20% by weight of the crude oxidation product. It is to be pointed out that the succinic acid may be separately purified and constitutes a valuable by-product.

In preparing the esters of this invention the glycol and/or polyglycol monoalkyl ether to be employed must be one in which the alkyl group of the ether is a radical having between 3 and about 12 carbon atoms per molecule. Preferably in order to obtain esters having extremely low pour points the alkyl radical will contain between about 3 and about 9 carbon atoms. 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 mixed ethers which are useable in preparing the esters of this

invention. The glycol or polyglycol group of the glycol monoalkyl ethers which have utility in preparing the esters of this invention will be ethylene glycol, propylene glycol, butylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol or tributylene glycol.

Thus compounds which may be used to form the ester lubricants of this invention 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.

It is observed that while all of the compounds of the classes mentioned will apparently form esters having relatively low pour points, high viscosity index and other desired characteristics described herein, making them useful as lubricants for the purposes described, certain of the compounds are superior to others in producing esters which are non-corrosive to particular metals. Thus 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 are substantially less corrosive to cadmium and copper.

The above or related glycol mono-ethers may be employed singly or 2 or more of the alcohols may be used in preparing an ester having the desirable characteristics.

The esters are preferably prepared directly from the crude oxidate or fraction thereof by reaction with the desired glycol mono-ether or mixture of such mono-ethers in the presence of a catalyst. In general one equivalent of acid fraction based on acid number will be reacted with between 1.1 and 1.5 equivalents of the glycol and/or polyglycol mono-ether. 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 ½ 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, phosphoric acid, hydrogen chloride, ethane sulfonic 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 term "pour point" as used herein is the temperature in °F. at which the material will flow and is determined by the method described in A. S. T. M. Standards on Petroleum Products and Lubricants, November 1950, page 50.

Although the esters described herein are oily liquids capable of being used as lubricants without modification it is often desirable to incorporate additives to improve oxidation stability, antirusting properties, extreme pressure characteristics, antiwear properties and the like. Agents which have been found to increase oxidation stability, i. e., to decrease viscosity increase, acid number increase and the like during use include zinc dioctyldithiophosphate, phenothiazine, carboxymethyl-mercaptosuccinic acid, ditertiarybutyl-p-cresol, p,p'-dioctyldiphenylamine, tetramethyldiamino - diphenylmethane, p,p'-diamino - diphenylmethane, 2 - salicylalaminophenol, propylgallate, phenyl-betanaphthylamine, N,N'-diphenyl-

salicylamide, triphenylamine, 2-amino-4-phenylphenol, 4-tertiarybutyl-2-phenylphenol, 4-ethylguiacol, 8-hydroxyquinoline, sulfurized terpenes and the like. These compounds may be used in amounts varying between about 0.1% and 2% by weight based on the final composition.

Agents which improve antirusting properties include particularly the metal sulfonates having excess metal base chemically combined or complexed therewith. Such sulfonates may be prepared by reacting sulfonic acids particularly oil-soluble petroleum sulfonic acids with between 1.1 and 2 or 3 equivalents of metal base at elevated temperatures preferably in mineral oil or petroleum thinner solution and in the presence of small amounts of water. Temperatures in the range of 150° F. to 500° F., preferably 220° F. to 450° F., are sufficient to effect the incorporation of excess base in a form in which it cannot be separated from the sulfonate solution by filtration. When lower temperatures are employed it is necessary to employ reduced pressures to permit removal of water during the reaction. The solubilized or complexed excess base is that amount present in the finished product over and above the amount which is chemically equivalent to the sulfonic acids present. Depending upon the particular metal oxide, hydroxide, or carbonate employed, the complex sulfonate may contain between 0.1 and 1 or 2 equivalents of excess metal.

In preparing these sulfonate complexes it is essential that all or substantially all of the water be eliminated from the reaction mixture. Thus in preparing barium complex sulfonate, employing typical conditions, a solution of one equivalent of oil-soluble petroleum sulfonic acids is heated and agitated with 2 equivalents of barium hydroxide and a small amount of water. The barium hydroxide may be added as a slurry in water. The mixture is heated to a final temperature of about 300° F. over a period of about 2 hours and the product filtered to remove any solid materials remaining. The resulting product is found to contain approximately 1.8 equivalents of barium per equivalent of sulfonic acids. Other alkaline earth metals, calcium, strontium and magnesium in the form of oxides, hydroxides or carbonates may be used in place of the barium hydroxide and will produce complex sulfonates having the desired characteristics. Also the alkali metals sodium, potassium and lithium in the form of hydroxides or carbonates may be employed in the same manner to obtain the complex sulfonates.

The complex sulfonates may be added to the synthetic lubricants of this invention in amounts between about 0.1% and about 15% by weight and preferably between about 0.5% and about 10% by weight based on the final composition.

Addition agents which impart extreme pressure characteristics to the ester lubricants of this invention include the sulfurized and phosphosulfurized fatty oils as for example sulfurized lard oil. These agents, which may be employed in amounts ranging between about 0.1% and 5% or 10% by weight, based on the finished oil, are well known in the mineral lubricating oil art and need not be further described herein.

Antiwear agents which may be employed include the organic phosphates and particularly the triesters of phosphoric acid. Thus tricresyl phosphate, octyldiphenyl phosphate, tri-2-ethylhexyl phosphate and like compounds perform the desired function in the ester lubricants of this invention.

The esters or mixtures of esters with low viscosity mineral lubricating oils may be used in the preparation of grease having desirable low temperature characteristics and yet having properties making them useful in applications where relatively high operating temperatures may be reached. Greases prepared from various esters described herein and from mixtures of such esters and low viscosity lubricating oil fractions of petroleum have been found to operate satisfactorily at temperatures as low as —75° F. and as high as 300° F. or even higher.

Suitable thickening agents which may be employed in preparing greases from the esters or mixtures of esters with mineral lubricating oil include soaps, such as the alkali and alkaline earth metal soaps, as well as aluminum soaps. Thus sodium, potassium, lithium, calcium, barium, strontium and magnesium soaps, as for example, the stearates, oleates, ricinoleates and the like may be employed to produce greases. Lithium stearate and lithium tallowate have been found to produce greases of exceptional quality. In addition to the simple soap greases, metal soap complexes consisting of complexes of metal soaps with, for example, metal carbonates, metal acetates and the like may also be employed to produce the greases of this invention. Such metal soap complexes are described in United States Patents 2,417,428 to 2,417,433, inclusive.

Other thickening agents which are particularly suitable include the silica and alumina aerogels and the alkyl ammonium bentonites in which at least one alkyl group is a long chain group, i. e., contains at least about 12 carbon atoms. Of the above non-soap thickeners, the silica aerogels appear to give the best greases.

In preparing soap greases, the soap is preferably separately prepared and then dispersed in the ester or mixture of ester and oil. The dispersion is obtained by heating the mixture of soap and oil to a temperature of at least about 225–350° F. and after mixing at this or high temperature the grease is cooled and the cold product worked to break down any gel structure and obtain the desired consistency. Where mixtures of mineral oil and esters are to be employed it is sometimes desirable to prepare the metal soap in the presence of part or all of the mineral oil and then add the ester which is thoroughly mixed into the soap-oil product.

In preparing greases with the non-soap thickening agents, such agents are milled into the ester or ester-oil mixture. This milling can be accomplished using an ordinary paint mill or colloid mill or equivalent milling device. Generally it is accomplished at about room temperature. In some instances, and in order to improve the water resistance of the aerogel type greases, the powdered aerogel may be treated with a water-proofing agent, as is well known in the art, prior to or after its incorporation into the ester or ester-oil mixture.

Still another class of thickening agents which may be employed with the esters of this invention, as well as with mixtures of the esters with mineral lubricating oil, consists of the metal phthalocyanines. Copper phthalocyanine is the preferred thickening agent of this class, however, other metal derivatives may be employed, such as the nickel, cobalt, iron, magnesium, calcium, etc., phthalocyanines. The preparation of greases using the phthalocyanines as thickening agents is illustrated in the specific examples. However, generally the method consists in mixing the phthalocyanine compound with the ester to be employed and milling the resulting mixture to obtain the desired degree of dispersion. This milling may be accomplished in a paint mill, a colloid mill or other equivalent milling device. Sometimes it is desirable, following the initial milling, to heat-treat the resulting product, for example by heating it to temperatures of about 250–450° F. and subsequently cooling and remilling the product. Greases prepared with the phthalocyanine thickening agents are observed to undergo no phase changes at temperatures between —105° F. and 390° F. making this class of greases particularly suitable for aircraft lubrication.

The amount of thickening agent, i. e., either the soap type or non-soap type, may be varied from approximately 3% to as high as 30–35% by weight of the finished grease depending upon the characteristics desired in the finished grease. Generally between about 10% and about 25% of thickening agent will be employed.

It is of course within the scope of this invention to incorporate oxidation inhibitors and/or stabilizing agents

in the greases. Although most of the well known inhibitors effect improvement it is found that dilauryl selenide is particularly effective in the greases described herein. Other compounds which may be employed include tetramethyl diaminodiphenyl methane, phenothiazine, ditertiarybutyl-p-cresol and phenyl alpha-naphthylamine.

Greases prepared from the esters of this invention using soap or non-soap thickeners of the types described hereinabove have been found to have extremely good oxidation resistance as indicated by standard oxidation stability test measurements. The test employed in this work is the one described in A. S. T. M. Standards on Petroleum Products and Lubricants, November 1950, page 402. This test involves placing 20 grams of the grease in a bomb and pressuring the bomb with oxygen to 100 pounds per square inch gage at a temperature of 210° F. The rate of pressure drop is indicative of the oxidation resistance of the grease under test.

To determine the ability of the greases of this invention to lubricate at low temperatures, grease samples were cooled for 16 to 20 hours in a closed container in a constant temperature box. The consistency of the grease at the low temperature was then estimated by hand working with a spatula. Temperatures of —75° F. to —105° F. were employed in this test work. In general, whereas grease containing only mineral lubricating oil as the oily component are either hard or brittle resins or stiff rubbery solids at such temperatures, the greases of this invention are capable of being worked at such low temperatures.

To determine the ability of greases to perform at high temperatures, a small sample of the grease was placed on a thermostatically controlled hot plate maintained at 390° F. and the heated grease was then worked on the hot surface with a spatula to determine its consistency.

The water resistance of greases prepared as described herein was determined by placing a small sample of the grease in boiling water and determining visually the effect of the water. Some of the greases of this invention, particularly those prepared with water resistant silica or alumina aerogels as well as those prepared with phthalocyanine and alkyl ammonium bentonites, were resistant to boiling water.

The following examples will serve to illustrate the invention but are not to be taken as limiting the broader aspects of this invention. In these examples the colors or the various products are referred to as Gardner colors. These colors were determined according to the method described in "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," Henry A. Gardner, seventh edition, 1935, page 191.

*Example I*

Approximately 14,000 grams of a refined paraffin wax having a melting point of about 145° F. and 80 grams of manganese 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. A sintered stainless steel disc having a pore size of approximately 10 microns was used as a means of obtaining a fine distribution of air in the mass being treated. The wax was heated to a temperature of 220° F. at a pressure of 100 pounds gauge, and air was introduced into the oxidation vessel at the rates shown below. The air rates shown are expressed in standard cubic feet per minute per 100 pounds of wax charge.

| Hours | Air Blowing Rate, Std. Cu. Ft./Min./100 lbs. Wax |
|---|---|
| 0-30 | 1.04 |
| 30-40 | 1.17 |
| 40-50 | 1.27 |
| 50-70 | 1.46 |
| 79-90 | 1.69 |
| 90-End of Run | 1.79 |



Acid number determinations were made on samples of the oxidized wax removed at intervals during the period of oxidation and the results of these tests were as follows:

| Hours | Acid No., mg. KOH/g. |
|---|---|
| 43 | 184 |
| 74 | 403 |
| 98 | 507 |
| 105 | 511 |
| 124 | 499 |

It will be observed that the acid number reached a maximum and started to decrease before air blowing was discontinued. The product consisted of liquid acids and a relatively large quantity of solid acids which separated from the liquid acids on cooling. The solid acids were very light in color and the liquid had a light amber color. This product appeared to be satisfactory as indicated by acid number and saponification number data. The saponification number was 625 mg. KOH/g. and the saponification number-acid number ratio was 1.26. The yield amounted to 12,725 grams or about 91% based on the wax charged to the oxidizer.

A representative sample of the cooled oxidized wax was centrifuged to separate the solid acids from the liquid acids. The solids separated in this manner amounted to 23.5% by weight of the crude product.

Approximately 4000 grams of the oxidation product of 499 acid number was stripped by heating to a temperature of 345° F. at 2 mm. pressure. The product had an acid number of 480 mg. KOH/g., a saponification number of 600 mg. KOH/g., and a saponification number-acid number ratio of 1.25.

*Example II*

Approximately 14,000 grams of a refined paraffin wax having a melting point of about 145° F. and 80 grams of manganese naphthenate were charged to a stainless steel oxidation vessel of the type described in Example I. In this case an automatic temperature control maintained temperatures during the oxidation at approximately 250° F., the maximum variation being between 248° F. and 255° F. The pressure was maintained at approximately 100 pounds gage. The air blowing rate was started at 0.65 standard cubic feet per minute and was gradually increased as the run progressed until the rate of 1.95 standard cubic feet per 100 pounds of charge was being used at the end of the oxidation. The air blowing was continued for a total of 139 hours at which time the product had an acid number of 569 mg. KOH/g. and a saponification number-acid number ratio of 1.25. The yield in this case amounted to 10,800 g. This product was extremely light in color (Gardner color 6 on a filtered sample) indicating the absence of polymerization and resinification during the oxidation. The viscosity of a filtered sample was 52.3 centistokes at 100° F. and 6.82 centistokes at 210° F. The product had a viscosity index of 91. The solid acids separated by centrifuging a portion of the oxidized product amounted to 25% by weight and after washing with toluene amounted to 19% by weight of the crude oxidation product. The washed material had a melting point of 328–345° F.

*Example III*

Approximately 14,073 grams of refined paraffin wax having a melting point of about 143–150° F. and 80 grams of manganese naphthenate was oxidized in the oxidation vessel employed in Example I. The temperature was maintained as nearly as possible at 250° F. and the maximum variations were between 212° F. and 256° F. During the major portion of the run, which was continued for a total of 143 hours, the maximum temperature variation was between 245° F. and 252° F. The air-blowing rates employed during the run were the same as those employed in Example I.

Acid number determinations made on samples of the oxidized wax removed at intervals during the period of oxidation and the results of these tests were as follows:

| Hours | Acid No., mg. KOH/g. |
|---|---|
| 72 | 321 |
| 90 | 419 |
| 115 | 515 |
| 123 | 539 |
| 139 | 551 |
| 143 | 576 |

The product was of a light amber color and had a saponification number of 720 and a saponification number-acid number ratio of 1.25. The yield was 12,000 grams.

*Example IV*

An oxidation run was carried out on 14,000 grams of purified paraffin wax having a melting point of 143–150° F. using 80 grams of manganese naphthenate as catalyst. The temperature was maintained between 220° F. and 250° F. and throughout the major portion of the run the temperature varied between 240° F. and 250° F. Air rates employed were identical with those used in Example I. Oxidation was continued for 134 hours at which time the acid number was 518 mg. KOH/g. and samples taken at intervals toward the end of the oxidation showed 507 mg. KOH/g. at 103 hours and 514 mg. KOH/g. at 111 hours. The product which amounted to 13,308 grams or approximately 95% based on the wax charge, had an extremely good color, a low viscosity, a saponification number of 648 mg. KOH/g., and a saponification number-acid number ratio of 1.25.

A portion of the above oxidate was stripped to remove materials boiling below the boiling point of succinic acid. This was accomplished by heating to a temperature of 347° F. at 5 mm. pressure. The topped or stripped oxidate had an acid number of 481, a saponification number of 605 and a saponification number-acid number ratio of 1.26. The material removed by distillation had an acid number of 629, a saponification number of 738 and a saponification number-acid number ratio of 1.17.

*Example V*

An oxidation run was carried out on 14,000 grams of 145° F. melting point refined paraffin wax using the conditions described in Example I. The time of air blowing was approximately 140 hours, and the product had an acid number of 550 mg. KOH/g. and a saponification number of 686 mg. KOH/g. This product consisted of a slurry of white crystals in a yellow oil of Gardner color 6.

A portion of the product was filtered at room temperature through a Buchner funnel. The unwashed filter cake of crude solid acids amounted to 31.3% of the crude oxidation product.

A second portion of oxidation product was filtered through canvas in a centrifugal filtration unit at 3500 R. P. M. using an 11 inch diameter basket (relative centrifugal force of 1900). This method gave more rapid filtration and a filter cake which contained less of the liquid acids. The yield of unwashed, solid acids amounted to 24.8% by weight of the original oxidized wax. This crude solid acid material had a melting point between about 286–315° F. The crude filter cake was repulped in an equal weight of toluene, filtered by suction and air dried to give a product melting between about 328° F. and 343° F. in a yield of 18% by weight based on the crude oxidation product. A single recrystallization from hot water raised the melting point of this product to approximately 360–368° F. This material is relatively pure succinic acid.



*Example VI*

An oxidation run was made to produce an oxidized product of relative low acid number for purposes of comparison with the products of this invention. In this case 14,000 grams of 143–150° F. melting point paraffin wax was oxidized under the conditions set forth in Example I for a total of 94 hours. At this time the product had an acid number of 382 mg. KOH/g., a saponification number of 535 mg. KOH/g., and a saponification number-acid number ratio of 1.40. Before removing the product from the oxidizer it was blown with nitrogen at atmospheric pressure to remove formic acid and the resulting product had an acid number of 379 mg. KOH/g.

This product was light amber in color and when cooled contained small quantities of white crystalline acids. The preparation of an ester from this oxidized product and the characteristics of this ester are shown in Example XXIV.

*Example VII*

The following oxidation run was made with an unrefined paraffin wax. The wax had a melting point of 180–190° F. and was dark brown in color. Analysis showed it to contain 0.11% sulfur, 0.025% nitrogen and approximately 0.6% oxygen.

Approximately 13,170 grams of the above wax and 80 grams of manganese naphthenate was charged to the oxidizer described in Example I. The temperature was maintained between 230° F. and 254° F. and during the greater portion of the time was at or near 250° F. The air-blowing rate was the same as that employed in Example I. The oxidation was continued for a total of 102 hours at which time the product had an acid number of 7.8 mg. KOH/g. and was extremely dark brown in color.

*Example VIII*

The following oxidation run was made in the oxidizer immediately following the run described in Example VII to show the inhibiting effect of small amounts of unrefined wax and/or oxidized unrefined wax on refined paraffin wax. Following the completion of the run described in Example VII the oxidizer was permitted to drain while hot so that the only material remaining in the oxidizer was that which did not drain from the oxidizer. The following run was made without cleaning the oxidation vessel.

To the oxidation vessel was charged 14,000 grams of refined paraffin wax having a melting point of 143–150° F. and 80 grams of manganese naphthenate. The temperature was maintained at approximately 250° F. and varied from 250 to 254° F. during the run. The air-blowing rate employed was the same as that used in Example I. The results of acid number determinations on samples removed at intervals during the oxidation were as follows:

| Hours | Acid No., mg. KOH/g. |
|---|---|
| 35 | 167 |
| 68 | 206 |
| 108 | 353 |
| 132 | 233 |

It is apparent that the above product is not satisfactory and does not meet the requirements for the acids of this invention. This product was a very dark brown sticky tar indicating that the course of the reaction changed after an acid number of around 350 had been reached so that the resulting product contained resin bodies and polymers in large proportions.

*Example IX*

Following the oxidation run described in Example VIII the oxidizer was drained and cleaned by washing with naphtha in order to remove as nearly as possible all

traces of the poorly oxidized wax obtained in Example VIII. To the clean vessel was charged 14,000 grams of refined paraffin wax having a melting point of 143–150° F. and 80 grams of manganese naphthenate and the oxidation of this material was effected at temperatures between 235 and 248° F. The air rate employed was the same as that described in Example I and the oxidation was continued for 122 hours. At this time the acid number of the product was 327 but the oxidized material was dark brown and extremely viscous indicating that the product contained high proportions of polymers and resinous bodies. This product was considered unsatisfactory and the oxidization was therefore not continued beyond 122 hours.

Following this run the oxidizer was again cleaned by washing with acetone and caustic followed by water and acetone, and subsequent runs made in the clean unit gave satisfactory products.

*Example X*

The following run was made to show the effect of high air blowing rates on the course of the oxidation. In this case 10,000 grams of refined paraffin wax having a melting point of 143–150° F. and 56 grams of manganese naphthenate were charged to the oxidizer and the oxidation was effected at temperatures of approximately 250° F. with a maximum variation between 230° F. and 258° F.

The air blowing rates employed were as follows:

| Hours | Air Blowing Rate, Std. Cu. Ft./Min./100 lbs. Wax |
|---|---|
| 0–45 | 1.77 |
| 45–52 | 2.95 |
| 52–200 | 3.63 |
| 200–245 | 2.5 |

The results of acid number determinations made on samples of the oxidized wax removed from the oxidizer during the period of oxidation were as follows:

| Hours | Acid No., mg. KOH/g. |
|---|---|
| 45 | 228 |
| 93 | 331 |
| 130 | 347 |
| 179 | 381 |
| 213 | 400 |
| 245 | 412 |

It will be noted that although the acid number was still increasing when the oxidation was discontinued the rate of increase was extremely low and it appeared that it would be impossible to obtain an acid number as high as 490 because the product had become dark and was very viscous indicating that polymerization and resinification were taking place. This product is not satisfactory and the run shows that high air rates, and particularly high initial air rates change the course of the oxidation and prevent the production of high acid number products.

*Example XI*

The following example shows the effect of permitting the temperature to rise above about 260° F. during the course of the oxidation. In this instance the wax charge and air blowing rates were the same as those employed in Example II and the oxidation was continued in the same manner as Example II up to 50 hours. At this time the automatic temperature control failed and the temperature gradually rose from about 250° F. to 280° F. at about 60 hours and 325° F. at 67 hours at which time the oxidation was discontinued. The product had an acid number of 280 mg. KOH/g. and was extremely dark and viscous. It was completely unsatisfactory for the purposes of this invention.



*Example XII*

This example shows the effect of permitting the temperature to rise above about 260° F. during the course of oxidation. In this case the temperature was permitted to rise to 290° F. for a short period of time and was then reduced to the desired range and the oxidation continued.

Approximately 14,000 grams of 143–150° F. melting point refined paraffin wax was oxidized using the air blowing rates set forth in Example I. Data regarding the temperature of operation and acid number of the material being oxidized are presented below:

| Hours | Air Blowing Rate, S. C. F./Min./100 lbs. | Temperature, ° F. | Acid No., mg. KOH/g. |
|---|---|---|---|
| 20 | 1.04 | 235 | |
| 23 | 1.04 | 270 | |
| 25 | 1.16 | 290 | |
| 38 | 1.16 | 241 | |
| 86 | 1.68 | 236 | 288 |
| 114 | 1.78 | 250 | 326 |
| 139 | 1.78 | 232 | 361 |
| 163 | 1.78 | 234 | 391 |
| 175 | 1.78 | 244 | 404 |

The oxidized product amounted to 13,800 grams of a material having a very dark brown color. This material had an acid number of 404, a saponification number of 647, and the saponification number-acid number ratio was 1.6. After permitting the succinic acid and other solid low molecular weight dicarboxylic acids to separate the supernatant oil had a kinematic viscosity of 251.4 centistokes at 100° F., 16.25 at 210° F. and a viscosity index of 65. The Gardner color of this oil was 17.

*Example XIII*

An ester was prepared by reacting 42.5 grams of oxidized paraffin wax having an acid number of 569 mg. KOH/g. (from Example II) with 101 grams of dipropylene glycol mono-isobutyl ether using 0.5 gram of stannous chloride dihydrate as catalyst. The mixture was diluted with approximately an equal volume of a paraffinic naphtha having a boiling range between about 200° F. and 300° F. and refluxed for 8.5 hours at a temperature ranging from about 185° F. to 300° F. with a water trap in the reflux line. At the end of this period of refluxing water formation had ceased. The resulting crude ester solution was diluted with an equal volume of low boiling paraffinic solvent (140° F. to 212° F.) and was percolated, at a temperature of 77° F., through a column of "Permutit DR," activated as described hereinabove with aqueous sodium hydroxide. The resin was then washed with additional quantities of the solvent. The effluent and washings were combined and passed through a steam heated vacuum stripper to remove solvent. The resulting oily ester was finished by vacuum distillation to a bottoms temperature of 320° F. at 2 mm. pressure. The resulting residuum was cooled and filtered by suction through a layer of diatomaceous earth.

The ester of wax acids with dipropylene glycol monoisobutyl ether produced as above had an acid number of 0.3 mg. KOH/g., a Gardner color of 7, a pour point of —66° F., a viscosity index of 113 and a kinematic viscosity of 100° F. of 13.9 centistokes.

*Example XIV*

An ester was prepared using 112 grams of the oxidized paraffin wax produced in Example II, 207 grams of ethylene glycol mono-(2-ethylbutyl) ether, 1.0 gram of stannous chloride dihydrate and 250 ml. of paraffinic naphtha. The preparation and purification of the ester was carried out in the manner described in Example XIII. The reaction time in this instance was 11.5 hours.

The ester of wax acids and ethylene glycol mono-(2-ethylbutyl) ether produced as above described had an

acid number of 0.24 mg. KOH/g., a Gardner color of 3, a pour point of —80° F., a viscosity index of 130 and a kinematic viscosity of 100° F. of 9.09 centistokes.

*Example XV*

An ester was prepared by reacting 86 grams of oxidized paraffin wax obtained in Example II and having an acid number of 569 mg. KOH/g. with 207 grams of dipropylene glycol mono-n-butyl ether. Two grams of stannous chloride dihydrate was employed as calatlyst and the mixture was refluxed in the presence of 200 ml. of the paraffinic naphtha described in Example XIII. Refluxing was continued for 13 hours at a temperature ranging from 265° F. to 330° F. The resulting crude ester product was purified in the manner described in Ex- Example XIII.

The resulting purified ester had an acid number of 1.1 mg. KOH/g., a Gardner color of 11, a pour point of —78° F., a viscosity index of 135 and a kinematic viscosity of 100° F. of 15.6 centistokes.

*Example XVI*

An ester was produced by reacting 79 grams of the oxidized paraffin wax produced in Example II with 211 grams of tripropylene glycol mono-n-butyl ether. Esterification was accomplished by refluxing this mixture in the presence of 250 ml. of paraffinic naphtha and 1.5 grams of stannous chloride dihydrate for a period of 19 hours at a temperature ranging between 250° F. and 320° F. The crude ester product was purified in the manner described in Example XIII.

The resulting purified ester had a Gardner color of 14, a pour point of —80° F., a viscosity index greater than 140 and a kinematic viscosity at 100° F. of 19.4 centistokes.

*Example XVII*

Example XVI was repeated using tripropylene glycol mono-isobutyl ether in place of tripropylene glycol mono-n-butyl ether. In this case the reaction time was 9.5 hours. The product, after purification, had a Gardner color of 9, a pour point of —75° F., a viscosity index of 138 and a kinematic viscosity at 100° F. of 215 centistokes.

*Example XVIII*

An ester was prepared by reacting 43.5 grams of the oxidized paraffin wax produced in Example II with 100 grams of dipropylene glycol mono-isopropyl ether. Esterification was effected by refluxing this mixture in the presence of 0.7 gram of stannous chloride dihydrate and 150 ml. of a paraffinic naphtha. Refluxing was continued for 12 hours, at which time the production of water had ceased. The maximum temperature reached during refluxing was 320° F. The crude ester product was purified in the manner described in Example XIII.

The resulting purified ester had an acid number of 1.2 mg. KOH/g., a Gardner color of 6, a pour point of —85° F., a viscosity index of 118 and a kinematic viscosity at 100° F. of 13 centistokes.

*Example XIX*

Example XVIII was repeated using dipropylene glycol mono-n-propyl ether in place of dipropylene glycol mono-isopropyl ether. The reaction time was 14 hours and the maximum temperature reached during refluxing was 320° F. After purification the resulting ester had an acid number of 1.2 mg. KOH/g., a Gardner color of 11, a pour point of —75° F., a viscosity index of 120 and a kinematic viscosity at 100° F. of 16.7 centistokes.

*Example XX*

An ester was prepared by reacting 328 grams of oxidized paraffin wax having an acid number of 569 mg. KOH/g. and 608 grams of ethylene glycol mono-(2-ethylbutyl) ether. Esterification was effected by refluxing this mixture in the presence of 3 grams of stannous chloride dihydrate and 250 ml. of a paraffinic naphtha at a temperature ranging between 250° F. and 310° F. for a total of 11 hours.

The crude ester without further dilution was percolated through a column of "Permutit DR" and the column effluent and washings stripped as described in Example XIII. The stripped residue was then filtered through diatomaceous earth.

The purified ester of wax acids and ethylene glycol mono-(2-ethylbutyl) ether had an acid number of 2.4 mg. KOH/g., a Gardner color of 7, a pour point of —90° F., a viscosity index of 128 and a kinematic viscosity at 100° F. of 10.8 centistokes.

*Example XXI*

An ester was prepared by reacting 1279 grams of oxidized paraffin wax produced in Example II with 1920 grams of ethylene glycol mono-n-butyl ether. Esterification was effected by refluxing this mixture in the presence of 9 grams of stannous chloride dihydrate and 1000 ml. of paraffinic naphtha for 19.5 hours at a temperature reaching a maximum of 280° F. The resulting crude ester was purified as described in Example XX.

The purified ester of wax acids and ethylene glycol mono-n-butyl ether had an acid number of 2.4 mg. KOH/g., a Gardner color of 12.5, a pour point of —90° F., a viscosity index of 118 and a kinematic viscosity at 100° F. of 15.6 centistokes.

*Example XXII*

An ester was prepared by reacting 360 grams of the oxidized paraffin wax produced in Example II with 793 grams of ethylene glycol mono-(2-ethylhexyl) ether. Esterification was effected by refluxing this mixture in the presence of 3.5 grams of stannous chloride dihydrate and 500 ml. of paraffinic naphtha for a total of 13 hours.

The crude ester product was decolorized by percolating it through a column of "Permutit DR" after diluting the crude product with an equal volume of paraffinic naphtha boiling in the range of about 200° F. to 300° F. The column was operated at a temperature of approximately 140° F. The effluent and washings from the column were stripped, topped and filtered in the manner described in Example XIII.

The resulting purified ester had an acid number of 3.0 mg. KOH/g., a Gardner color of 9.5, a pour point of —85° F., a viscosity index of 120 and a kinematic viscosity at 100° F. of 15.6 centistokes.

*Example XXIII*

An ester was prepared by reacting 125 grams of oxidized paraffin wax produced as in Example II and having an acid number of 569 mg. KOH/g. and 174 grams of propylene glycol mono-n-butyl ether. Prior to use in this case the oxidized paraffin wax was stripped to a bottoms temperature of 345° F. at 5 mm. pressure. Esterification was accomplished in the presence of 0.9 gram of stannous chloride dihydrate and 50 ml. of paraffinic naphtha by refluxing for a total of 12.5 hours, at which time the production of water had ceased. The crude ester product was purified following the method described in Example XXII and the resulting purified product had a Gardner color of 12, a pour point of —75° F., a viscosity index of 107 and a kinematic viscosity at 100° F. of 16 centistokes.

*Example XXIV*

For purposes of comparison with the ester oils of this invention and in order to show the undesirability of employing wax oxidation products obtained under conditions such that the maximum acid number is less than about 490 mg. KOH/g., an ester was prepared following the method outlined in Example XIX using the oxidized paraffin wax produced as described in Example VI, which wax had an acid number of 379 mg. KOH/g. The crude

ester product was purified as described in Example XVIII and the resulting product had a pour point of —5° F. making this oil unsatisfactory for use at low temperatures.

*Example XXV*

The ester products of some of the above examples were subjected to a test designed to determine the oxidation resistance and the resistance to corrosion of various metals under conditions highly conducive to oxidation. The test conditions employed are those described in test No. 530.8.2 described in Federal Specification VV–L–741*d*, "Lubricants, Liquid Fuels, and Related Products; Methods of Inspection Sampling and Testing." The test involves passing air at a controlled rate of 5 liters per hour through a 100 ml. sample of the oil maintained at 250° F. under reflux, for a period of 168 hours, in the presence of five different metal catalysts in the form of 1 inch square panels. The metals employed included magnesium alloy, aluminum alloy, copper, cadmium plated steel and steel. Data regarding the appearance and weight change of the metals at the end of the test are shown in the following tabulation. Since none of the oils tested showed appreciable corrosive effect on aluminum alloy or steel, the results of tests on these metals are not included in the table.

| Ester Product of Example No.— | Appearance and Wt. Change, mg./cm² | | |
|---|---|---|---|
| | Mg Alloy | Cu | Cd Plated Steel |
| XIII | Bright +0.08 | Etch and Stain −2.0. | Plating Removed −2.8. |
| XIV | Slight Stain +0.19. | Slight Stain +0.03. | Slight Etch +0.40. |
| XV | Slight Stain −0.19. | Slight Stain −0.13. | Bright −1.4. |
| XVI | Bright 0.00 | Stain −0.20 | Slight Stain −0.20. |
| XIX | Bright +0.05 | Slight Stain −0.75. | No Effect. |

In addition to the above data, tests were made on the oil before and after the oxidation test to determine viscosity increase and color change of the esters. It is to be noted that none of the oils showed sludging or deposition of gums. Data regarding viscosity increase and color change during the test is shown in the following table:

| Ester Product of Example No.— | Kinematic Viscosity, Centistokes at 100° F. | | Gardner Color | |
|---|---|---|---|---|
| | Before | After | Before | After |
| XIII | 12.09 | 53.69 | 7 | Dark Green |
| XIV | 9.09 | 19.83 | 3 | 8 |
| XV | 15.56 | 17.26 | 7 | 7 |
| XVI | 19.44 | 40.23 | 13 | 13 |
| XIX | 16.69 | 26.92 | 11 | 16 |

*Example XXVI*

A lithium stearate grease was prepared using 25 grams of a commercial lithium stearate and 75 grams of the ester of dipropylene glycol mono-n-butyl ether with wax acids, produced in Example XV. This mixture was heated in an open vessel with stirring to a temperature of 375° F. At this point a clear melt was obtained. The resulting melt was chilled rapidly and then mechanically worked by passing it three times, at room temperature, through a three roll paint mill with a roll separation of approximately 0.001 inch. A smooth buttery grease was obtained.

The product when cooled to —75° F. was soft and somewhat rubbery. It melted to form a liquid at approximately 390° F. In the oxidation resistance test described hereinabove a pressure drop of 5 pounds per square inch gage was observed in approximately 20 hours.

A second grease prepared in the same way, except that it contained 1% by weight of commercial dilauryl selenide, had the same properties as the above grease, except for oxidation resistance. In this case a pressure drop of 5 pounds was observed after approximately 70 hours.

*Example XXVII*

A calcium grease prepared in the manner described in Example XXVI, using calcium stearate in place of lithium stearate, has a good grease body and is satisfactory for use at relatively high and relatively low temperatures.

*Example XXVIII*

Example XXVI repeated using sodium stearate in place of lithium stearate gives a grease similar in most respects to that produced with lithium stearate.

*Example XXIX*

Example XXVI repeated using as the oil ingredient 25 grams of a low viscosity mineral lubricating oil (SAE 5W grade) and 50 grams of the ester of dipropylene glycol mono-n-butyl ether with wax acids, produced a grease having properties which are in general similar to the grease without mineral oil. However, this product is somewhat harder at —75° F. and the oxidation resistance was somewhat poorer than the corresponding grease without mineral oil.

*Example XXX*

A silica-ester oil grease was prepared using a hydrophobic silica having a particle size of 0.01 micron or smaller, with the ester produced in Example XIV. In this case 75 grams of the ester of ethylene glycol mono-(2-ethylbutyl) ether with wax acids and 17 grams of the powdered silica were mixed at ordinary temperatures to form a stiff dry mass. The product was passed through a three roll paint mill with a roll separation of approximately 0.03 inch and then the milling was repeated twice with a roll separation of 0.001 inch. A smooth, tan colored, translucent grease was obtained.

The product stiffened somewhat on cooling to —75° F. but it was still easily worked at that temperature. This product softened but did not melt at 390° F., it resisted immersion in boiling water and was completely unaffected after 4 hours of such treatment. In the oxidation resistance test a pressure drop of 5 pounds per square inch gage was observed after 15 hours.

A second grease prepared in the identical manner, except that it contained 1% by weight of commercial dilauryl selenide, showed a pressure drop in the oxidation test of less than 3 pounds per square inch gage at 100 hours.

*Example XXXI*

A silica-ester oil grease was prepared using a commercial silica aerogel having a particle size of 0.5 to 1.0 micron and the ester oil produced in Example XVI. In this case a mixture of 89 grams of the ester and 11 grams of the silica aerogel was compounded as described in Example XXX to form a smooth, stiff, opaque grease. This product became stiff but remained grease-like at 390° F. and it was easily worked at —75° F.

*Example XXXII*

A silica-ester oil grease was prepared using a water-repellent silica aerogel and the ester oil product of Example XV. The water-repellent aerogel was an aerogel which had been pretreated with a modified alkyd resin, the resin being one modified by producing in the presence of a fatty acid, i. e., linoleic acid.

A mixture of 85 grams of the ester and 15 grams of the water-repellent silica aerogel having a particle size of 0.5 to 1.0 micron together with 0.5 gram of dilauryl selenide was milled as described in Example XXX. A smooth, stiff, translucent, light tan grease was obtained. It was

unaffected by immersion in boiling water for 4 hours. In the oxidation resistance test a pressure drop of 5 pounds per square inch gage was observed after approximately 50 hours.

*Example XXXIII*

Example XXXII was repeated using the ester oil produced in Example XVI in place of the ester of Example XV and gave a grease very similar in characteristics to the one produced in Example XXXII.

*Example XXXIV*

A grease was prepared from a mixture of 75 grams of the ester produced in Example XVIII and 25 grams of an alkyl ammonium bentonite, the latter being a commercial product known as Bentone 34 obtainable from the Bariod Sales Division of the National Lead Company, Los Angeles, California.

This mixture was mechanically stirred to form a soft mass which was then milled as in Example XXVI to form a smooth, stiff, opaque, light gray grease. On cooling to —75° F. the product was soft and somewhat rubbery. It resisted immersion in boiling water for five minutes and in the oxidation resistance test a pressure drop of 5 pounds per square inch gage was observed in approximately 40 hours.

This grease preparation was repeated with the addition of 1 percent of tetramethyldiaminodiphenyl methane. This latter grease showed a pressure drop of 5 pounds per square inch gage after approximately 75 hours in the oxidation resistance test.

*Example XXXV*

A phthalocyanine-ester oil grease was prepared using 20 grams of copper phthalocyanine, 79 grams of the ester produced in Example XV and 1 gram of dilauryl selenide. The copper phthalocyanine was of a quality considered suitable for grease production and was obtained from Organic Chemicals Division, Du Pont de Nemours Company, Wilmington, Delaware. The copper phthalocyanine was heated to a temperature of 435° F. for a period of 3.5 hours prior to incorporating it into the grease. Following this heat treatment the copper compound was cooled and added to the ester and antioxidant. High speed stirring produced a thick slurry. The slurry was milled in a three roll paint mill with a roll separation of 0.001 inch until the product had a smooth grease consistency. The milled product was heated for 2 hours at a temperature of approximately 400° F. and then cooled. The product was then reduced to a final stable consistency by passing it through the paint mill with the rolls set at the clearance indicated hereabove.

The resulting grease was a deep blue, smooth, soft product. It was easily worked at —75° F., softened slightly but retained its grease body at 390° F. and was water resistant as indicated by its ability to withstand boiling water for 30 minutes. In the oxidation resistance test a pressure drop of less than 2 pounds per square inch gage was observed after 100 hours.

I claim:

1. An ester suitable for use as a lubricant, said ester being prepared by esterifying a compound selected from the class consisting of the monoalkyl ethers of glycols and polyglycols with a mixture of acids comprising dicarboxylic acids, said mixture of acids being obtained by air blowing a refined paraffin wax having a melting point between about 120° F. and about 165° F. at a temperature between about 210° F. and 260° F. until the acid number of the oxidized wax is between 490 and 575 mg. KOH/g., the rate of air blowing being initially between about 0.75 and about 1.25 standard cubic feet per minute per 100 pounds of wax and being gradually increased until the rate is between about 1.5 and about 2.0 standard cubic feet per minute per 100 pounds of wax after about 90 hours of oxidation.

2. An ester suitable for use as a lubricant, said ester being the product obtained by esterifying a compound selected from the class consisting of the monoalkyl ethers of glycols and polyglycols with an acid mixture comprising dicarboxylic acids, said acid mixture having a saponification number-acid number ratio between about 1.2 and about 1.32 to 1 and being obtained by air blowing a refined paraffin wax having a melting point between about 120° F. and about 165° F. at a temperature between about 210° F. and 260° F. until the acid number of the oxidized wax is between 490 and 575 mg. KOH/g., the rate of air blowing being initially between about 0.75 and about 1.25 standard cubic feet per minute per 100 pounds of wax and being gradually increased until the rate is between about 1.5 and about 2.0 standard cubic feet per minute per 100 pounds of wax after about 90 hours of oxidation.

3. An ester according to claim 2 in which said refined paraffin wax is one having a melting point of 143–150° F.

4. A lubricant comprising an ester of a compound selected from the class consisting of the monoalkyl ethers of glycols and polyglycols having between about 3 and about 12 carbon atoms in the alkyl group with an acid mixture having a saponification number-acid number ratio between about 1.2 and about 1.32 to 1 and being obtained by air blowing a refined paraffin wax having a melting point between about 120 F. and about 165° F. at a temperature between about 210° F. and about 260° F. and a pressure between atmospheric pressure and 500 pounds per square inch until the acid number of the oxidized wax is at least about 490 mg. KOH/g., the rate of air blowing being initially between about 0.75 and about 1.25 standard cubic feet per minute per 100 pounds of wax and said rate being increased as the oxidation proceeds to between about 1.5 and 2.0 standard cubic feet per minute per 100 pounds of wax at 90 hours, said last named rate being maintained to the end of the period of oxidation.

5. A lubricant according to claim 4 in which said lubricant is a lubricating oil having a pour point between —50° F. and —100° F. and a kinematic viscosity between about 3 and about 35 centistokes at 100° F.

6. A lubricant according to claim 4 in which said refined paraffin wax is one having a melting point of 143–150° F. and said temperature of air blowing is between about 230° F. and about 250° F.

7. An ester lubricating oil suitable for use at sub-zero temperatures and having a pour point between about —30° F. and about —100° F., a kinematic viscosity between about 3 and about 35 centistokes at 100° F. and a viscosity index between about 95 and about 150, said ester lubricating oil being prepared by esterifying one equivalent of an acid mixture comprising dicarboxylic acids with between about 1.1 and 1.5 equivalents of a compound selected from the class consisting of the monoalkyl ethers of glycols and polyglycols having between about 3 and about 12 carbon atoms in the alkyl group, said acid mixture having a saponification number-acid number ratio between about 1.2 and about 1.32 to 1 and being obtained by air blowing a refined paraffin wax having a melting point between about 120° F. and about 165° F. at a temperature between about 210° F. and 260° F. until the acid number of the oxidized wax is between 490 and 575 mg. KOH/g., the rate of air blowing being initially between about 0.75 and about 1.25 standard cubic feet per minute per 100 pounds of wax and being gradually increased until the rate is between about 1.5 and about 2.0 standard cubic feet per minute per 100 pounds of wax after about 90 hours of oxidation.

8. An ester lubricating oil according to claim 7 in which said compound is a glycol monoalkyl ether having between about 3 and about 9 carbon atoms in the alkyl group.

9. An ester lubricating oil according to claim 8 in which said glycol monoalkyl ether is ethylene glycol mono-(2-ethylbutyl) ether.

10. An ester lubricating oil according to claim 7 in which said compound is a polyglycol monoalkyl ether having between about 3 and about 9 carbon atoms in the alkyl group.

11. An ester lubricating oil according to claim 10 in which said polyglycol monoalkyl ether is diethylene glycol mono-n-butyl ether.

12. A lubricating grease suitable for use at sub-zero temperatures, said grease consisting of a lubricating oil containing between about 3% and about 35% by weight of a thickening agent selected from the class consisting of metal soaps, silica and alumina aerogels, alkyl ammonium bentonites and metal phthalocyanines, said lubricating oil comprising an ester having a pour point between −30° F. and −100° F., a kinematic viscosity between about 3 and about 35 centistokes at 100° F. and being obtained by esterifying an acid mixture having a saponification number-acid number ratio between about 1.2 and about 1.32 to 1 with a compound selected from the class consisting of the monoalkyl ethers of glycols and polyglycols, said acid mixture being obtained by air blowing a refined paraffin wax having a melting point between about 120° F. and about 165° F. at a temperature between about 210° F. and about 260° F. and a pressure between atmospheric pressure and 500 pounds per square inch until the acid number of the oxidized wax is at least about 490 mg. KOH/g., the rate of air blowing being initially between about 0.75 and about 1.25 standard cubic feet per minute per 100 pounds of wax and said rate being increased as the oxidation proceeds to between about 1.5 and 2.0 standard cubic feet per minute per 100 pounds of wax at 90 hours, said last named rate being maintained to the end of the period of oxidation.

13. A grease according to claim 12 in which said thickening agent comprises lithium stearate.

14. A grease according to claim 12 in which said thickening agent comprises copper phthalocyanine.

15. A grease according to claim 12 in which said thickening agent comprises an alkyl ammonium bentonite.

16. A method of preparing a lubricant from paraffin wax which comprises air blowing a refined paraffin wax having a melting point between about 120° F. and about 165° F. at a temperature between about 210° F. and about 260° F. and a pressure between atmospheric pressure and 500 pounds per square inch until the acid number of the oxidized wax is at least about 490 mg. KOH/g., the rate of air blowing being initially between about 0.75 and about 1.25 standard cubic feet per minute per 100 pounds of wax and said rate being increased as the oxidation proceeds to between about 1.5 and 2.0 standard cubic feet per minute per 100 pounds of wax at 90 hours, said last named rate being maintained to the end of the period of oxidation and esterifying the oxidized paraffin wax with a compound selected from the class consisting of the monoalkyl ethers of glycols and polyglycols having between about 3 and about 12 carbon atoms in the alkyl group.

17. A method of preparing a lubricating grease from paraffin wax which comprises air blowing a refined paraffin wax having a melting point between about 120° F. and about 165° F. at a temperature between about 210° F. and about 260° F. and a pressure between atmospheric pressure and 500 pounds per square inch until the acid number of the oxidized wax is at least about 490 mg. KOH/g., the rate of air blowing being initially between about 0.75 and about 1.25 standard cubic feet per minute per 100 pounds of wax and said rate being increased as the oxidation proceeds to between about 1.5 and 2.0 standard cubic feet per minute per 100 pounds of wax at 90 hours, said last named rate being maintained to the end of the period of oxidation, esterifying the oxidized wax product with a compound selected from the class consisting of the monoalkyl ethers of glycols and polyglycols having between about 3 and about 12 carbon atoms in the alkyl group, and incorporating in the resulting ester between about 3% and about 35% by weight of a thickening agent selected from the class consisting of metal soaps, silica and alumina aerogels, alkyl ammonium bentonites and metal phthalocyanines.

18. A method according to claim 17 in which said thickening agent is a metal soap and said thickening agent is incorporated in said ester by heating the mixture to a temperature of at least about 225° F., cooling the resulting mixture and working the product to obtain a grease structure.

19. A method according to claim 17 in which said thickening agent is a non-soap thickening agent and is incorporated in said ester by milling at ordinary temperatures.

20. A lubricant according to claim 4 comprising between about 10% and about 75% of said ester in a mineral oil fraction.

21. A lubricant according to claim 4 in which said lubricant is a grease consisting of said ester to which is added between about 3% and about 35% by weight of a thickening agent selected from the class consisting of metal soaps, silica and alumina aerogels, alkyl ammonium bentonites and metal phthalocyanines.

22. A lubricant according to claim 4 containing also between about 0.1% and about 15% based on the final composition of an antirusting agent consisting of a metal sulfonate having 0.1 to 2 equivalents of excess metal base complexed therewith per equivalent of metal sulfonate.

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