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PROCESS FOR THE EXTRACTION OF MINERAL OIL CONTAMINANTS FROM SYNTHETIC LUBRICANTS

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6 Claims. (Cl. 260—485)

The present invention relates to a process for the removal of mineral oil which has contaminated synthetic lubricants, involving the use of the lower aliphatic carboxylic acids as solvents. The synthetic lubricants with which this invention is concerned are those of the complex ester-diester type, such as are described hereinafter, but the invention will work equally well with lubricants consisting of complex esters or diesters by themselves.

Current development in aircraft engines, particularly the "prop-jet" type require special properties from the lubricating medium, particularly where machanisms other than the engine itself have to be lubricated by the same medium. The very high operating temperatures generated in these engines together with the very low ambient temperatures which may result from high altitude operation means that the lubricant must maintain its good lubricating properties over a very wide range of temperatures, and in addition should have a low pour-point and a high viscosity index (or low A. S. T. M. slope) so that it may have a sufficiently high viscosity at engine temperatures coupled with a sufficiently low viscosity at the ambient temperatures.

Mineral oils do not provide the properties required to meet the requirements of aviation gas turbines as described above. A typical mineral oil may have the following properties:

Kinematic viscosity at 210° F. cs	9
Kinematic viscosity at 100° F. cs	67.5
A. S. T. M. slope (100–210° F.)	0.688
Flash point, °F	415
Pour point, °F	—10

Synthetic lubricants have recently been developed which meet the requirements of the aviation engines mentioned above, particularly the types comprising mixtures of complex esters with diesters. Although each of these ester types is capable of functioning as a lubricant alone, for aviation purposes the best result is obtained by a blend of complex esters and diesters. A typical synthetic lubricant of this type may have the following properties:

Kinematic viscosity at 210° F. cs	8.5
Kinematic viscosity at 100° F. cs	41.8
Kinematic viscosity at —40° F. cs	14,900
A. S. T. M. slope (100–210° F.)	0.582
Flash point, °F	440
Pour point, °F	below —60

Complex esters form a class that is particularly suitable for thickening diesters as, unlike many polymers, they are relatively highly oxygenated, and are, therefore, readily soluble in diesters. In addition they are themselves good lubricants and may be used without other major components.

Complex esters are here meant to include esters containing more than 3 residues of an acid, alcohol, polybasic acid or polyhydric alcohol and in which there is

at least one polyhydric alcohol and one polybasic acid residue each of which has at least two of its functional groups esterified. They are formed by the esterification, in one or more stages, of mixtures of multifunctional acids and multifunctional alcohols with or without monofunctional acids, monofunctional acids and alcohols, or monofunctional alcohols. They may also be formed from compounds which contain both hydroxy- and carboxy-groups, and the complex ester class includes all those compounds in the molecule of which at least two residues, each with a plurality of esterifiable groups, has at least two or such groups esterified. Where present, the monofunctional components normally provide the terminal groups and their proportion in the esterification mixture determines the average number of multifunctional acid and alcohol groups that will be present in the final complex ester molecule. In many cases the theoretical molecular structure of the complex ester molecule may represent an average only, individual molecules differing widely in chain length and configuration. In general it is preferred to employ aliphatic materials, and in any case the esters should be free from olefinic unsaturation.

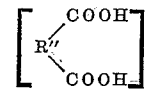
A useful class of complex esters may be represented by the general formula:

$$R_1—OOC—R_2—COO—R_3—OOC—R_4—COOR_5$$

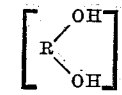
In particular a type of complex ester which has been found particularly useful in aviation synthetic lubricants may be represented as follows:

$$R'OOC—R''—COO—R—OOC—R''—COOR'$$

A particular form of this ester may be made by reacting together under esterification conditions and in one or more stages two molar proportions of a dicarboxylic acid



two molar proportions of an aliphatic alcohol (R'OH) and one molar proportion of a polyglycol



wherein the acid is sebacic and/or adipic acid, the alcohol is a branched chain monohydric C_8 or C_9 saturated aliphatic alcohol or a mixture in which such alcohols predominate, and the polyglycol is a polyethylene glycol up to and including hexaethylene glycol or a polyethylene glycol fraction whose average molecular weight does not substantially exceed that of hexaethylene glycol.

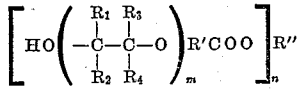
Sebacic acid is preferred, with a mixture of sebacic and adipic second, and adipic alone third. The preferred polyglycols in order are tetraethylene glycol (commercial Polyglycol 200), commercial triethylene glycol and hexaethylene glycol (commercial Polyglycol 300). The preferred branched chain alcohol is 2-ethyl hexanol, while C_8–C_9 branched chain OXO alcohols also give excellent results. Branched chain C_8–C_9 alcohols from other sources such as "higher alcohol mixture H 1623" (commercially available) or capryl alcohol may also be used and give good results.

Other types of complex esters may be formed by fully esterifying a dicarboxylic acid of the formula:

$$R(COOH)_2$$

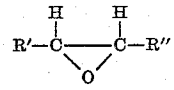
where R is a hydrocarbon radical containing 0–26 carbon atoms or an organic radical consisting of a series of saturated aliphatic hydrocarbon radicals linked by at least one noncarbon atom of the group consisting of oxygen and sulphur, the total number of carbon atoms and said non-

carbon atoms in the radical being 3 to 80, in which there are at least 2 carbon atoms between each pair of said non-carbon atoms and a total of not more than 2 sulphur atoms, with a hydroxy ester of the form:

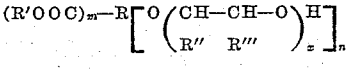


where R′ is an organic radical selected from the group consisting of (1) aliphatic hydrocarbon radicals containing 1 to 22 carbon atoms, and (2) radicals consisting of two aliphatic hydrocarbon groups interlinked by one atom of the group consisting of oxygen and sulphur, the total number of carbon atoms in the radical being from 2 to 22; where R″ is an organic radical selected from the group consisting of (1) aliphatic hydrocarbon radicals containing from 1 to 20 carbon atoms, and (2) radicals consisting of a series of saturated aliphatic hydrocarbon radicals linked through 1 to 5 non-carbon atoms of the group consisting of oxygen and sulphur, each hydrocarbon radical so linked by a non-carbon atom containing at least 2 carbon atoms, the total number of carbon atoms and said non-carbon radicals being from 4 to 20, the total number of sulphur atoms in the radical being not greater than 2; R_1, R_2, R_3 and R_4 each represent a member of the group consisting of hydrogen and alkyl groups containing 1 to 2 carbon atoms each; m is an integer from 1 to 20, n is either 1 or 2.

Another class of complex ester relates to products formed by reacting aliphatic esters of open chain aliphatic carboxylic acids containing one to three carboxyl groups and one or more hydroxyl group, the esterifying radical being any open chain aliphatic hydrocarbon group (which may contain one or more hydroxyl group) with an alkylene oxide of the formula:



Such products have the general formula:



where R′ is an open chain aliphatic hydrocarbon group, which may or may not contain one or more hydroxyl group, R is an open chain aliphatic hydrocarbon group, R″ is hydrogen or an alkyl or alkylene group containing not more than 6 carbon atoms, R‴ is hydrogen or a methyl group, m is an integer from 1 to 3, n is an integer, x is an integer from 1 to 30.

A further type of complex ester is of the form:

R″OOCRCOOR′OOCR‴

prepared by reacting one mole of a dibasic acid with one mole of a glycol in such a manner that a half ester is formed, after which the terminal hydroxyl and carboxyl groups are esterified with a monobasic acid and monohydric alcohol, respectively.

Another type of complex ester is prepared by reacting, under esterification conditions, two moles of a monobasic aliphatic acid with two moles of a glycol and one mole of a dibasic aliphatic or aromatic acid. These complex esters may be represented by the general formula:

$R_2COOR_1OOCR_3COOR_1OOCR_2$

Generally it is preferred that the complex ester and diester components should comprise materials chosen from glycols and polyglycols having 2 to 60 carbon atoms, alcohols having up to 30 carbon atoms, dicarboxylic acids having from 2 to 20 carbon atoms and monocarboxylic acids having up to 30 carbon atoms.

Although complex esters outlined above may be used as lubricants by themselves, their particular viscosity characteristics may preclude their use alone under the special conditions of modern aviation use. For example, many

of these complex esters are thick fluids that would be unsuitable as lubricants, certainly at low temperatures and some complex esters are in fact solids. Also the type of complex ester that may be produced most cheaply from available raw materials is, commonly, not the most suitable as a lubricant. However, certain complex esters when liquid are known to have extremely good lubricating properties.

It is known that the good lubricating properties of complex esters are to some extent bestowed on blends containing them in admixture with certain synthetic oleaginous fluids.

The lighter component of such ester blends is an oleaginous liquid preferably containing ether oxygen or thioether sulphur linkages. Thus it may be a simple ester wherein either the acid or the alcohol or both contain the required linkages, it may be a diester of a glycol and one or more carboxylic acids and, again, the ether linkages can be in either or both components. Preferably the lighter component is an ether, particularly a glycol ether. The glycol may be any aliphatic glycol but it is preferably a polyalkylene glycol. Polyalkylene glycols suitable for use in the ethers under consideration have the general formula HO—R—OH, where R may contain at least one ether oxygen or thioether sulphur atom in the chain connecting the hydroxy groups and where there is an aliphatic hydrocarbon radical of at least 2 carbon atoms between either hydroxy group and the nearest ether atom thereto and wherein any ether atom is separated from the nearest other ether atom by an aliphatic hydrocarbon group of at least 2 carbon atoms. Preferably the aliphatic hydrocarbon groups are substituted ethylene groups and particularly useful glycols are those made by condensing ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol or 1,2 or 2,3 butylene glycol or 1,1′-butylene glycol alone or in admixture with any one or more of these glycols. A particularly preferred glycol is obtained from mixed polymerised ethylene oxide and propylene oxide in proportions between 1:3 and 3:1. These glycols, of course, may be modified by substitution of hydrogen atoms with hydrocarbon groups. The glycols may be used alone as diluents or may be etherified with one or more alcohols or mercaptans, preferably aliphatic alcohols or mercaptans.

The total number of carbon, oxygen and sulphur atoms in the light component should be less than 70 and there should be no more than 2 sulphur atoms. The number of oxygen atoms should not be so great that the liquid is substantially water soluble.

Another class of suitable blending compounds with complex esters are diesters of aliphatic dicarboxylic acids, such as sebacic, adipic or other such acids together with aliphatic alcohols, including OXO alcohols. It has been found that such blends may be prepared which have better properties than the complex esters themselves. In other words, when a minor proportion of a diester of low viscosity and high A. S. T. M. slope is blended with a complex ester of high viscosity and low A. S. T. M. slope, the resulting lowering of the viscosity of the complex ester is more marked than the corresponding increase of the A. S. T. M. slope. It is further found that the lubricating properties, failure loads and other significant properties of the blends are not significantly different from those of the complex esters themselves.

Synthetic lubricants, including the complex ester-diester type may oxidise in service particularly where employed under severe service conditions. It is known, however, that oxidation may be retarded by the use of certain additive materials.

The additive materials that may be used may be classified to fall into five groups thus:

(1) Aromatic nuclear alcohols, including mono-, di- or tri-hydric phenols, substituted products thereof in particular alkyl and alkoxy substituted phenols, bis phenols and the like.

(2) Aromatic nitro compounds such as nitrated phenols and nitro-benzenes.

(3) Aromatic amines and aliphatic primary amines including phenolic amines, primary, secondary and tertiary and mixed amines and amides.

(4) Organic sulphur compounds particularly thio-alcohols, thio-amides, cyclic compounds containing bivalent sulphur such as thiophenes and thiazoles, and amine sulphides and, in particular, thio-diphenylamine (diphenyl thiazine).

(5) Organic compounds containing both phosphorus and sulphur such as thiophosphates, and reaction products of phosphorus sulphides and organic materials such as mineral or natural oils, terpenes and the like.

The synthetic lubricants described above have proved satisfactory in service, but the present high cost of production makes it desirable that such lubricants should be reclaimed after use. In particular there may be some deterioration in their properties due to contamination by mineral oil during use. This deterioration can be in the viscosity characteristics, and also some increase in the acidity of the synthetic lubricants. While the latter can be restored to the desired level by alkali-washings, it is the object of this invention to restore the required temperature-viscosity characteristics when affected by mineral oil contamination by treating the contaminated lubricant with certain highly oxygenated compounds described hereinafter.

Of many samples of used synthetic lubricants examined by the inventor the majority have been found to contain mineral oil contaminations, the order generally being below 5%. It has been found that as little as 2% of mineral oil may result in serious contamination of the temperature-viscosity characteristics, and Table I shows the effect of such quantities of a typical mineral oil having a viscosity at 210° F. of about 57 SUS, designated Oil A, on a synthetic lubricant (designated SL) of the complex ester-diester type.

TABLE I

	SL	SL+1% Oil A	SL+2% Oil A	SL+5% Oil A
Kinetic Viscosity, cs.:				
at 210° F	7.79	7.72	7.72	7.71
at −40° F	11,900	12,500	14,500	29,700

In considering the problem of removing the mineral oil from used lubricants, it is not possible to use ordinary petroleum solvents to extract the mineral oil because of the mutual solubilities of the diester components of the lubricant and the mineral oil. The discovery has been made, however, that if aliphatic carboxylic acids containing from 1 to 6 carbon atoms are used as solvents for synthetic lubricants effective separation of the contaminated mineral oil from the synthetic lubricant may be achieved with restoration of the viscosity-temperature characteristics. The solubility of the synthetic ester in the solvent may be from 5% upwards, and preferably from 50% upwards.

In particular, if acetic acid, which is an aliphatic saturated monocarboxylic acid, either glacial or containing minor proportions of water is used as a solvent, the mineral oil contaminants are effectively insoluble while the ester or diester components are completely soluble.

The invention may be carried out with acetic acid, for example, as the solvent, by shaking vigorously the contaminated lubricant with not less than 1 volume of glacial acetic acid or acetic acid containing up to 15% by volume of water, and allowing the mixture to stand until the mineral oil phase separates, the solution of lubricant in solvent then being separated from the mineral oil layer.

The synthetic lubricant may be removed from the solvent by water washing using not less than ⅓ volume of water, and preferably 1 volume of water, to ensure phase separation taking place. The two phases of lubricant and acid are then separated, preferably with the aid of an emulsion-breaker such as methylol. It is usually preferable to water-wash a second time.

It may be necessary after this treatment to reduce the acidity of the extracted lubricant, and this may conveniently be achieved by a sodium carbonate wash using about 1 volume of a 10% solution of sodium carbonate. Again it is preferable to use an emulsion-breaker in conjunction with the alkaline wash. This neutralising treatment should be followed by a water wash. The final acidity of the extracted lubricant should be less than 0.1 mg. KOH/grm. A final stripping should be carried out to remove emulsion-breaker and water.

If the properties of the synthetic lubricant are not fully restored by the above treatment, this may be repeated as required.

The diluted acid remaining from the process may be concentrated, i. e. by distillation.

The invention therefore comprises a process for the separation of a mixture of a synthetic lubricant and a mineral oil comprising contacting the said mixture with an aliphatic carboxylic acid containing from one to six carbon atoms per molecule, whereby the synthetic lubricant dissolves in the said acid and forms therewith a separate phase from the mineral oil, separating the said lubricant/acid phase from the mineral oil and extracting the said synthetic lubricant from the said acid.

Having described the invention, this may be more particularly understood by reference to the following examples.

Example I

To illustrate the efficacy of mineral oil removal from synthetic lubricants containing small amounts of mineral oil, one volume of glacial acetic acid was shaken with one volume of used synthetic lubricant of the complex ester-diester type, which was suspected of mineral oil contamination. An upper layer of oil separated out, which was water washed to remove acids and taken up in 40/60 petroleum ether and extracted, the petroleum ether being flashed off. The volume of the layer was about 3% of the initial synthetic lubricant.

To illustrate the efficacy of the separation, the following data are given on the refractive indices and saponification numbers of the unused synthetic lubricant, unused mineral oil, and the extracted layer.

TABLE II

	Upper Extracted Layer	57 secs. SUS Mineral Oil (DED 2479)	Unused Synthetic Lubricant
Refractive Index n_D^{20}	1.479	1.484	1.450
Saponification No.	65	2.0	280

These data indicate a mineral oil content of about 80–90% in the upper layer. The mineral oil nature of upper layer was confirmed by infra-red analysis, and optical density measurements on the spectrum gave an estimate of 5–20% synthetic lubricant present in the mineral oil layer. Since this layer itself was only 3% of the volume of the original used oil, the synthetic lubricant loss due to the separation is negligible.

A further addition of two volumes of acetic acid resulted in a further 1% separation of mineral oil, after which the synthetic lubricant appeared free from contamination.

Example II

The restoration of the viscosity-temperature characteristics of a mineral oil contaminated synthetic lubricant of the complex ester-diester type is shown in Table III. Acetic acid was used as the solvent and it was found that

the viscosity properties were completely restored after the second acetic acid extraction.

TABLE III

Temperature of Kinetic Viscosity measurements	Used Synthetic Lubricant	After 1st Acetic Acid Treatment	After 2nd Acetic Acid Treatment	Unused Synthetic Lubricant
210° F.	8.35	8.18	7.58	7.5
−40° F.	26,300		12,000	13,500

What I claim is:

1. A process for the removal of mineral oil from synthetic ester lubricating oil compositions which have become contaminated with mineral oil wherein said synthetic oils are polycarboxylic acid esters consisting of hydrocarbon chains joined by ester groups, said chains being selected from the group consisting of aliphatic hydrocarbon chains and aliphatic hydrocarbon chains containing ether linkages therein, which comprises the steps of contacting the said contaminated synthetic lubricating oil with a substantially anhydrous aliphatic saturated hydrocarbon monocarboxylic acid containing from 1 to 6 carbon atoms per molecule, whereby the synthetic ester lubricating oil dissolves in said acid and forms therewith a phase separate from the mineral oil, separating the two phases so formed and extracting the synthetic lubricating oil from said acid phase.

2. A process for restoring the viscosity temperature characteristic of synthetic ester lubricating oil which has become contaminated with mineral oil, wherein said synthetic oil is a polycarboxylic acid ester consisting of hydrocarbon chains joined by ester groups, said chains being selected from the group consisting of aliphatic hydrocarbon chains and aliphatic hydrocarbon chains containing ether linkages therein, which comprises the steps of contacting said contaminated synthetic lubricating oil with an anhydrous aliphatic saturated hydrocarbon monocarboxylic acid containing from 1 to 6 carbon atoms per molecule, whereby the synthetic lubricating oil dissolves in said acid and forms therein a phase separate from the contaminating mineral oil, separating the two phases so formed, and repeating the process until the viscosity temperature characteristics of the synthetic lubricating oil are restored to about their original values before contamination with mineral oil.

3. A process according to claim 1 wherein said synthetic lubricating oil comprises a blend of a complex ester formed by reacting together at least three materials selected from the group consisting of monobasic acids, monohydric alcohols, polybasic acids, and polyhydric alcohols, with an ester formed by reacting together a dibasic acid and an aliphatic alcohol.

4. A process according to claim 1 wherein said synthetic lubricating oil comprises a blend of a complex ester formed by reacting together two mols of an aliphatic alcohol, two mols of an aliphatic dibasic acid, and one mol of a glycol with a simple ester formed by reacting together two mols of an aliphatic alcohol with one mol of an aliphatic dibasic acid.

5. A process according to claim 4 wherein said aliphatic alcohol is 2-ethyl-hexanol, wherein said dibasic acid is sebasic acid, and wherein said glycol is a polyethylene glycol.

6. A process according to claim 1 wherein said anhydrous acid is glacial acetic acid.

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