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SUGAR ESTER-CONTAINING LUBRICANT COMPOSITIONS

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The present invention relates to improved lubricating oil compositions and pertains more particularly to lubricating oil compositions which are especially effective as crankcase lubricants for gasoline engines.

In the early development of compounding lubricating oils, the art was faced with the problem of ring-sticking in certain diesel engines and solved the problem by incorporating into the crankcase lubricant, agents having detergent-dispersant properties which promoted engine cleanliness. Since then the art has been primarily concerned with this problem of engine cleanliness in diesel engine service, and in attacking the problems in gasoline engine lubricants the art has tended to use the same compounding agents.

This approach to gasoline engine lubricating problems by analogy to diesel engine service should be expected to yield satisfactory results. As a matter of fact, crankcase lubricants compounded with diesel engine additives have, under certain conditions, given improved performance as compared to uncompounded oils.

However, the problem of providing completely satisfactory lubrication for gasoline engines has in recent years become more difficult to solve, and has been found that often incomplete protection is obtained with diesel engine compounding agents. One of the factors contributing to this increased difficulty is that not only has there been an increased demand lately for motor gasoline which tends to expand the use of less desirable stocks, but also the demand for high quality aviation gasoline has increased, likewise relegating to motor gasoline the less stable hydrocarbons such as olefins and cracking products. Further, recent changes in gasoline engine design including higher compression ratios and smaller clearances have aggravated the deleterious effects of engine deposits such as piston lacquer or surface varnish throughout the engine. For instance, hydraulic valve lifters are often found to be partially or completely stuck by deposits, irrespective of whether such deposits are composed of hard or soft carbon, and particular attention must be given to the crankcase lubricant in order to avoid deposition of material in the valve lifters and the damage resulting from such deposits.

As indicated above, the expected completely satisfactory performance of diesel engine detergent-dispersant additives in gasoline engine crankcase lubrication is not borne out in operation, especially in operation under city driving conditions, to which family automobiles are mainly subjected. With the understanding that the following is not given by way of limitation but only for the purposes of illustration, it can be said that the need for compounding agents different from those used in diesel lubricants may follow from the two apparently-significant differences between diesel and gasoline engines. First, piston temperatures in diesel engines are high, in the neighborhood of 400° F., which promote lubricating oil degradation, whereas in gasoline engines subjected to normal city driving conditions, the piston temperatures are low, of the order of 275° F. from the ring zone and down to about 175° F. on the piston skirt. With respect to blow-by in diesel engines, compression works against air only, and during the firing stroke a turbulent and heterogeneous mixture is burned in all parts of the combustion chamber; therefore, diesel engine blow-by is mainly exhaust gases and air. However, in gasoline engines, the compression stroke works against a relatively

homogeneous fuel-air mixture and the flame propagation during the firing stroke is such as to force fuel-air mixture against the piston crown; therefore, gasoline engine blow-by does not consist of exhaust gases, but mainly fuel gases which contain partially oxygenated organic compounds. These blow-by fuel gases appear to be the major cause of deposits in gasoline engines, and oxidative deterioration of the lubricating oil, such as occurs at the high temperatures in diesel engines, does not seem to be an appreciable factor.

For optimum performance, not only must the compounding agents minimize the tendency of the products formed in gasoline engine operation to deposit out on the engine surfaces, but also the agents themselves must not contribute to the formation of deleterious products which may tend either to promote pre-ignition (and hence require gasoline of a higher octane rating to avoid knocking) or to clog narrow passages and thus intertere with the operation of close-fitting parts. Since many of the metal-containing additives are notable offenders in these several respects, particularly as regards the pre-ignition phenomenon, the choice of suitable additives for gasoline crankcase lubricants is preferably restricted to non-metallic compounds.

In view of all these factors, it is not surprising that the compounding agents which give good performance in diesel engine service do not effectively minimize the deposition of varnish and lacquer-like materials in gasoline engines operated under city driving conditions. In fact, in many cases the additives employed in diesel lubricants have been found to increase the amounts of these deposits which are formed in gasoline engine service.

The present invention is based on the discovery that by incorporating a minor percentage of a higher aliphatic acid ester of a sugar in a substantially wax-free oil of lubricating viscosity, there is obtained a novel lubricant composition which satisfies all of the requirements indicated above and is especially effective for promoting engine cleanliness in gasoline engines operating under city driving conditions. Thus, it has been found that, quite unexpectedly, the addition of but relatively small amounts of these esters to the oil inhibits the formation of lacquer and varnish on the piston and other exposed surfaces much more effectively than is the case with even diesel type lubricants containing sufficiently large amounts of compounding ingredients as to pass the Supplement II Test, the most rigorous test for diesel lubricants. The advantageous effects of the present sugar ester additives do not appear to reside in any change in the nature of the deposits formed on the piston and other surfaces; rather, the action of the new agents is apparently attributable to their ability to prevent the potential lacquer- and varnish-forming materials from depositing out on the piston surfaces and adjacent areas.

The sugar esters whose use falls within the scope of this invention can be defined as those wherein at least one hydroxyl group of a mono-, di- or trisaccharide is esterified with an aliphatic carboxylic acid containing 10 or more carbon atoms. Suitable sugars which can be employed in forming the esters are, for example, erythrose, threose, xylose, arabinose, rhamnose, mannose, galactose, glucoheptose, fructose, sorbose, glucodecose, lactose, sucrose, maltose, cellobiose, raffinose, rhamninose, and melicitose.

Representative higher (i. e., containing 10 or more carbon atoms) aliphatic carboxylic acids which can be employed to form the above-described esters include capric, undecyclic, lauric, tridecoic, oleic, myristic, palmitic, stearic, arachidic, behenic and melissic, as well as the higher naphthenic acids and naphthenic acid mixtures of the type derived from petroleum. Again, mixtures of acids derived from such natural sources as coconut oil, lard oil, tallow, cottonseed oil, soybean oil and palm oil can be used.

Also suitable for use in the present invention are mixed sugar esters of the type which contain two or more different acyl groups attached to a given sugar molecule. In the case of these mixed esters, at least one of the acyl groups must be that of a higher aliphatic acid of the type defined above, while one or more of the remaining acyl groups may, if desired, be that of a lower

carboxylic acid, as for example formic, acetic, propionic, butyric, valeric, caproic or caprylic acids.

Among the higher aliphatic acids, a preferred group comprises those containing 10 or more carbon atoms which have a single olefinic carbon-to-carbon double bond, as exemplified by 9-undecylenic, 4-tetradecylenic, oleic, palmitoleic, ricinoleic, elaidic, petroselinic, erucic and brassidic acids.

While the acids employed in forming the esters of the present invention have been referred to as "aliphatic" in character, the term "aliphatic acids" is also intended to include acids of the type defined above which are substituted by one or more of various groups such as phenyl, hydroxyl, amino, alkoxy, chloro and the like, particularly when the number of such substituent groups is not such as to alter the essentially aliphatic character of the acyl group present in the sugar ester compound. The term also includes higher cycloaliphatic acids, as for example, the various naphthenic acids of higher molecular weight, as well as p-octylcyclohexane corboxylic and similar acids.

Representative sugar ester compounds which can be employed with success in the practice of the present invention include erythrose monooleate, arabinose monooleate, arabinose distearate, arabinose dioleate, xylose diricinoleate, glucose trioleate, glucose pentaoleate, glucose monostearate, glucose monooleate monoricinoleate, glucose monomelissate, glucose tripalmitoleate, glucose trimyristoleate, sucrose monooleate, sucrose tetraoleate, sucrose dimelissate, sucrose pentaarachidate, sucrose monopalmitoleate, sucrose monobutyrate dioleate, sucrose monoricinoleate, sucrose dioleate monopalmitate, fructose dioleate, fructose mononaphthenate, fructose tripalmitate, fructose monoacetate monooleate, fructose trioleate dicaprate, sorbose monostearate, sorbose dipalmitate, lactose monooleate, lactose monooleate monostearate, maltose monoacetate dioleate, maltose trioleate, rhaminose pentaoleate and raffinose trioleate.

For the purposes of the present invention, the desired improvement in the anti-deposition characteristics of the base oil can be obtained by the addition of a minor percentage of one or more of the sugar-ester compounds described above. Thus, good results have been obtained by the addition of a total of from about 3.5 to 20% by weight of the esters, though amounts less than about 3% are not appreciably effective. Conversely, amounts larger than about 25% by weight are seldom employed except in the case of lubricating compositions which are primarily intended to be combined with more dilute (i. e., less highly compounded) lubricating oils.

The compounding agents of this invention can be used with good effect in the case of any substantially wax-free base oil stock. Thus, said stock can be a dewaxed Pennsylvania or other paraffin base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or non-hydrocarbon oil of lubricating viscosity. As synthetic oils there can be mentioned alkylated waxes and similar alkylated hydrocarbons of relatively high molecular weight, hydrogenated polymers of hydrocarbons and the condensation products of chlorinated alkyl hydrocarbons with aryl compounds. Other suitable oils are those which are obtained by polymerization of lower molecular weight alkylene oxides such as propylene and/or ethylene oxide. Still other synthetic oils are obtained by etherification and/or esterification of the hydroxy groups in alkylene oxide polymers such as, for example, the acetate of the 2-ethylhexanol-initiated polymer of propylene oxide. Another important class of synthetic oils comprises the high molecular weight esters as, for example, di(ethylhexyl) sebacate.

Satisfactory crankcase lubricant compositions for use in low temperature gasoline engine service can be obtained by adding to the base oil only one or more of the sugar esters as disclosed herein, or by adding said esters to the oil in conjunction with other additives such as pour point depressants, oiliness agents, extreme pressure additives, anti-oxidants, corrosion inhibiting agents, blooming agents, thickening agents and compounds for enhancing the viscosity index of the oil. Again, while for low temperature gasoline engine operation it is preferred to employ lubricating oil compositions which are free from metal-containing compounds, the use of lubricants incorporating metal-containing additives also falls within the broader scope of the invention. Thus, in some cases the conjoint use of metal salt detergents (e. g., polyvalent metal phenates, sulfonates, thiophosphates, and the like) and said sugar esters will result in the desired high degree of protection against engine deposits without over-stepping the maximum metal content permitted for efficient engine operation.

The present invention is illustrated in various of its embodiments by the following example:

EXAMPLE

In this operation various lubricating oil compositions are tested as crankcase lubricants in a Chevrolet 6-cylinder engine operated using a low grade gasoline especially prone to cause engine deposits, the conditions being those defined in the standard FL–2 test procedure as described in the June 21, 1948 report of the Coordinating Research Council. This procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2500 R. P. M. and 45 brake horsepower for 40 hours. At the end of the test, the engine is dismantled and the amount of engine deposits on the piston is determined and expressed as the average piston rating. This value is obtained by visually rating (on a scale of 0 to 10, with 10 representing the absence of any deposit) the amount of deposit on each piston skirt and averaging the individual ratings so obtained for the various pistons.

In the case of the base oil alone without the addition of any additives (the base oil employed being a highly refined, wax-free base oil of SAE 30 grade, having a V. I. of 85 and derived from California waxy crude) it is found that the average piston rating is approximately 3.0. With the same base oil compounded with diesel engine lubricating oil-type commercial additives to a level equivalent to Series 1 lubricants (Army Specification 2–104B, Supplement I), the average piston rating obtained is 6.7. On the other hand, as indicated by the data presented in the table below, when the base oil is compounded with the indicated amounts of a sugar ester, greatly superior engine cleanliness is obtained.

Table

	Average piston rating No.
Base oil+10% fructose dioleate	7
Base oil+10% sorbose pentaoleate	7
Base oil+10% arabinose monooleate	8.5
Base oil+10% arabinose dioleate	9.5
Base oil+10% sucrose tetraoleate	9.7
Base oil+10% glucose pentaoleate	9.8
Base oil+2% glucose pentaoleate	4.0
Base oil+4% glucose pentaoleate	6.2
Base oil+5% glucose distearate	7.5
Base oil+5% glucose monoricinoleate distearate	8.0

While the lubricant compositions described in this application are particularly well adapted for use as crankcase lubricants in gasoline engines operated under city driving or other conditions involving periodic operation at relatively low temperatures, the said compositions are also well suited for other uses. Thus, they can be employed as electrical insulating oils, cable oils, turbine oils and the like, as well as in aircraft engines and in other types of internal combustion engines.

We claim:

1. A gasoline engine crankcase lubricant composition comprising a major portion of a substantially wax-free oil of lubricating viscosity and a total of from about 4 to 10% by weight of a saccharide selected from the group consisting of pentoses, hexoses and sucrose in which at least one hydroxyl group is esterified with an aliphatic carboxylic acid having at least 10 carbon atoms in the molecule, said lubricant composition having the ability to effectively inhibit the formation of deleterious deposits in gasoline engines operated at the relatively low temperatures of city driving conditions.

2. A gasoline engine crankcase lubricant composition comprising a major portion of a substantially wax-free oil of lubricating viscosity and a total of from about 4 to 10% by weight of a saccharide selected from the group consisting of pentoses, hexoses and sucrose in which at least one hydroxyl group is esterified with an aliphatic carboxylic acid containing at least 10 carbon atoms and having a single olefinic carbon-to-carbon double bond in the molecule, said lubricant composition having the ability to effectively inhibit the formation of deleterious deposits in gasoline engines operated at the relatively low temperatures of city driving conditions.

3. A gasoline engine crankcase lubricant composition comprising a major portion of a substantially wax-free oil of lubricating viscosity and a total of from about 4 to 10% by weight of glucose pentaoleate, said lubricant composition having the ability to effectively inhibit the formation of deleterious deposits in gasoline engines operated at the relatively low temperatures of city driving conditions.

4. A gasoline engine crankcase lubricant composition comprising a major portion of a substantially wax-free oil of lubricating viscosity and a total of from about 4 to 10% by weight of sucrose tetraoleate, said lubricant composition having the ability to effectively inhibit the formation of deleterious deposits in gasoline engines operated at the relatively low temperatures of city driving conditions.

5. A gasoline engine crankcase lubricant composition comprising a major portion of a substantially wax-free oil of lubricating viscosity and a total of from about 4 to 10% by weight of arabinose dioleate, said lubricant composition having the ability to effectively inhibit the formation of deleterious deposits in gasoline engines operated at the relatively low temperatures of city driving conditions.

6. A gasoline engine crankcase lubricant composition

comprising a major portion of a substantially wax-free oil of lubricating viscosity and a total of from about 4 to 10% by weight of fructose dioleate, said lubricant composition having the ability to effectively inhibit the formation of deleterious deposits in gasoline engines operated at the relatively low temperatures of city driving conditions.

7. A gasoline engine crankcase lubricant composition comprising a major portion of a substantially wax-free oil of lubricating viscosity and a total of from about 4 to 10% by weight of arabinose monooleate, said lubricant composition having the ability to effectively inhibit the formation of deleterious deposits in gasoline engines operated at the relatively low temperatures of city driving conditions.

References Cited in the file of this patent

UNITED STATES PATENTS

2,115,823	Miller et al.	May 3, 1938
2,138,771	Pevere	Nov. 29, 1938
2,564,423	Barnum	Aug. 14, 1951
2,580,036	Matuszak	Dec. 25, 1951