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TOP CYLINDER LUBRICANT

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The present invention relates to lubricant compositions, and is more particularly concerned with lubricant compositions adapted to be introduced into the combustion chambers of internal combustion motors with or in the presence of the fluid fuel. The compositions of the present invention consist, in essence, of solutions of mixtures of saturated, aliphatic oxygen-containing products of mineral hydrocarbon origin in suitable mineral hydrocarbon oils, and are suitable for dissolution in gasoline to produce a motor fuel known in the trade as "lubricated gasoline".

In my Patent No. 1,828,356 for "Process of producing water-insoluble petroleum-soluble carboxylic acids and the product thereof" there was described a process for the liquid-phase, controlled partial oxidation of hydrocarbons or mixtures thereof such as those occurring in petroleum. According to that patent, such hydrocarbon mixtures were subjected to the described oxidation treatment with the result that there was produced an oxidation reaction mixture comprising a great many different types of oxygen-containing compounds together with hydrocarbons which had not become oxidized during the treatment. It was there stated that this oxidation procedure produced material amounts of acids, i. e., saponifiable carboxylic acids soluble in petroleum and in the reaction mixture, which acids could be separated from the reaction mixture and be employed as softening agents in coating compositions containing nitro-cellulose. According to that patented procedure, the non-acidic, i. e., not readily saponifiable, portions of the reaction mixture were returned to the oxidizer where, admixed with a complementary portion of fresh charge, they were again subjected to the oxidation treatment.

I have now found that the partial oxidation reaction mixtures and products derivable therefrom possess properties which adapt them for use as lubricant aids, and, particularly, properties which make them peculiarly adapted for use in "top-cylinder lubricants". These mixtures of partially oxidized, saturated, aliphatic hydrocarbons and unoxidized hydrocarbons have been found to have solvent effects with respect to a number of substances; in particular, they are good solvents for the pitch which, together with road dirt and other materials, largely forms the so-called "carbon" in internal combustion engines. Moreover, these mixtures, which are freely soluble in oils, e. g., lubricating oils, in all proportions, have been found to have the peculiar property of enhancing the lubricating values of oils so that films of the latter are strengthened and their internal friction lessened. Likewise they lend high penetrative qualities to oils, causing the latter to enter particularly narrow spaces: it may be said that they increase the capillarity of oils.

A particularly valuable property of the top cylinder lubricants of the present invention is their capacity to remove from the combustion space lead compounds produced therein by the burning of fuel containing lead in combined form, e. g., lead tetraethyl.

A further, "negative", property of these top cylinder lubricants is their inability to etch metal surfaces. It is a fact, that upon continued use in an engine, lubricating oils generally, and selective-solvent-refined Pennsylvania base oils particularly, develop serious etching properties upon certain types of metals, e. g., cast iron, steel, cadmium silver, and probably the commonly employed "bearing metals". Corrosion or etching also may occur from the combustion products of sulphur contained either in the oil or in the fuel or in both, from carbon dioxide plus residual moisture (condensed in the combustion space on cooling of the motor), from combustion products of halogen compounds in the oil or in the fuel, and from phosphoric acid compounds contained either in the oil or in the fuel. The top cylinder lubricants of the present invention, or at least constituents thereof, segregate at the surface of the metal on which they are used and to a very considerable degree prevent etching and materially retard corrosion by the corrosion agencies above mentioned.

The lubricant composition of the present invention comprises, then, a solution of a relatively small but effective amount of the aforesaid oxidation mixture (to be described hereinafter in greater particularity) in a petroleum oil vehicle suitable, as to viscosity, penetrativeness and the like, for introduction into the combustion chamber of an internal combustion engine, which vehicle may be, and preferably is, a mixture of light oil such as "300 oil" or "mineral seal oil" and light lubricating oil such, for instance, as the Coastal oil product known as "200 pale oil". Illustrative of what is meant here by "a relatively small but effective amount of the lubricant aid", and illustrative as well of one embodiment of the present invention is a solution composed of:

	Percent
(a) The aforesaid lubricant aid	3
(b) Mineral seal oil	25
(c) 200 pale oil	72

That is to say, a lubricant composition of the present invention is characterized (disregarding the lubricant aid) by the presence of a material amount of a light hydrocarbon oil having of itself low lubricating properties and a major amount of a lubricating oil of a relatively light grade, which latter component preferably is of South Texas or Coastal origin because of its low

Conradson carbon and because it of itself tends to dissolve "carbon" in the combustion chamber.

The lubricant composition, when admitted into the combustion chamber, has been found adapted to lubricate the top rings of the piston, the cylinder wall, and especially the lips and necks of the valves of the motor; it tends to remove already deposited "carbon" and lead deposits from the chamber and to prevent the formation of further "carbon" and lead compounds; and it tends to free sticky valve stems and to prevent sticking of the latter. Because of its wetting properties towards the lips of the valves, it improves the compression of, and retards corrosion by, the gaseous combustible mixture of the motor. Furthermore, I have found that the lubricant composition in no wise injures or depreciates the value of the crankcase oil in those cases where it succeeds in passing the oil rings of the piston.

While the lubricant composition of the present invention may be introduced into the combustion chamber of the engine in any way found desirable, I prefer to introduce it with the motor fuel. Accordingly, I admix a relatively small amount of the composition with gasoline, in which latter it dissolves perfectly. A preferred mixture is a "lubricated gasoline" produced by dissolving 1 gallon of the lubricant composition in 200 gallons of gasoline (i. e., gasoline containing 0.5% by volume of the lubricant composition). This proportion may be varied within a wide range, according to the particular conditions encountered: thus, the lubricant composition may amount to 1.0% or more of the lubricated gasoline, or it may in certain instances amount to but about 0.25% by volume of the lubricated gasoline although generally it will be found that in such high dilution as is represented in the latter formula the results are not so definite.

The manner in which I prepare the lubricant aid (*a*) referred to hereinbefore is as follows:

As the starting material upon which the oxidation treatment is to be performed I use a petroleum hydrocarbon mixture such as 36–40 fuel oil distillate, or 150 neutral oil, or 200 neutral oil, or Coastal oils, or the like, but preferably the first named. The 36–40 fuel oil distillate may have been derived from Mid-Continent or pipeline crude oil or from Pennsylvania crude, in which latter event it may have a cold test of about 40° F. (solid) thus showing the presence of a considerable quantity of low melting-point paraffin wax, or may be the product obtained by redistilling or reducing what is known as "light pressed oil."

The fuel oil distillate (or other starting material) is heated to about 130° C. and, in the presence of a suitable catalyst (e. g., manganese oleate) or accelerator of oxidation, e. g., non-acidic oxidation products of a previous charge, is subjected to treatment with a free oxygen-containing gas (such as air, oxygen-enriched air, or oxygen) in finely subdivided state by forcing streams of the said gas in the form of fine bubbles upwardly through a column of the starting material maintained within a suitable chamber adapted to withstand pressure. As the starting material begins to oxidize the temperature of the charge sharply rises; undue increase in temperature is avoided by the use of suitable cooling means (e. g., cooling coils), the temperature not being allowed to rise above 150–160° C. A super-atmospheric pressure of up to 350 pounds per square inch, preferably 250 pounds per square inch, is maintained within the chamber, gaseous or vaporous materials accumulating at the top of the column being withdrawn continuously or intermittently.

This oxidation treatment may be, and preferably is, continued until the total mass within the chamber shows a quantity of acids approximating 30% by volume, although continuance of oxidation to this precise acids content is not critical. When this general stage of oxidation has been reached, the oxidation is discontinued and the reaction mixture is removed from the oxidizer. The reaction mixture thereafter may be treated to reduce the free acids content thereof, and may if desired be additionally treated to separate unoxidized hydrocarbons from the mixture.

According to one embodiment of the invention I use as the lubricant aid in the top cylinder lubricant all of the non-acidic ingredients of the crude oxidation reaction mixture, said mixture comprising, in addition to some unoxidized (and unchanged) hydrocarbons, a plurality of alcohols, ketones, alcohol-ketones, lactones and esters produced by the oxidation as aforesaid of the hydrocarbonaceous starting material. These oxygen-containing bodies are saturated aliphatic compounds. In preparing such a lubricant aid mixture I prefer to proceed as follows: The crude reaction mixture from the oxidizer is treated with sufficient caustic soda solution to neutralize all of the free acids contained therein. Thereafter, the neutralized acids are separated out, leaving a non-acidic residue which is the lubricant aid referred to hereinbefore. It consists of, besides some unchanged hydrocarbons, alcohols, ketones, alcohol-ketones, lactones and esters, the combined lactone and ester content representing from about 12 to about 20% of the total non-acidic residue. The said residue has a specific gravity which is lower by about 3 to 5° Baumé than the original starting material: where the starting material is 30% distillable at 340° C., the said residue will be found to be 70% distillable at the same temperature. Where the starting material shows a 5% solubility in 96% sulphuric acid the said residue shows a solubility of from about 25 to about 35% in the same test. The aniline point of the said residue lies within the range of 58 and 68, usually about 65, whereas the aniline point of the original starting material normally is about 92.

It will be apparent, from the foregoing, that the above-described lubricant aids may be combined with the light oil and the light lubricating oil in proportions other than those indicated in the specific example, and that the vehicle for the non-acidic residue may consist of one oil (instead of a mixture of oils), so long as there is produced a composition which is of sufficiently low gravity and viscosity to be penetrative and so long as the composition contains the said non-acidic residue in sufficient concentration to effect the aforesaid results. I have found that the content of said non-acidic residue may be increased to about 10% of the composition; also, that in certain cases (as, for instance, where the pressure and temperatures to be encountered are not extremely high), the vehicle may simply consist of "300 oil" or mineral seal oil in the absence of any so-called lubricating oil. Where a mixture of light (penetrative) oil and lubricating oil is used as the vehicle, the relative proportion between these two components may be varied within wide limits: thus, depending upon their respective physical properties, they may be used in varying proportions up to, say, 75 parts of the light oil to 25 parts of the lubricating oil, or vice versa.

Where a light oil is used in admixture with an oil of lubricating grade as the vehicle, I have found that the evaporation of the lighter oil in the combustion chamber by absorption of heat serves to protect the lubricating oil and to some extent to prevent undesired evaporation of the said non-acidic residue. Also the composition of the present invention is intended to produce a slow counter-current against the rising of crankcase oil into the combustion chamber, thereby preventing the accumulation of carbon from such crankcase oil.

According to another embodiment of the invention the top cylinder lubricant may consist essentially of a solution, in an appropriate lubricating oil (or mixture of oils at least one of which has lubricating properties), of a mixture of oil-soluble synthetic esters derived from the saturated aliphatic carboxylic acids produced by carrying out the oxidation procedure aforesaid. That is to say, a preferred form of my invention consists in the use, in gasoline or similar internal combustion engine fuel, of oil-soluble, saturated, petroleum acid esters in conjunction with a lubricating oil. In accordance therewith I may extract self-formed esters from the crude oxidation reaction mixture, or I may extract the free acids content of the latter and convert said acids into their corresponding esters, using the esters as substantially the sole lubricant aids.

Substantially equally effective as lubricant aids in the present relation have been found to be:

1. Mixtures of the aforesaid alkyl esters with non-acidic constituents of the oxidation reaction mixture;
2. The oxidation reaction mixture after the free acids contained therein have been esterified by an esterification procedure practiced upon the whole mixture without any separation; and
3. The whole oxidation reaction mixture containing up to 20–30% acids.

Thus, I have discovered that it is not strictly necessary to remove the acids from the crude oxidation reaction mixture, it being a surprising fact that the acids—containing crude oxidation reaction mixture—containing even as much as 20–30% free acids—when used as the lubricant aid of the top cylinder lubricant composition of the present invention functions as satisfactorily as the above-discussed neutral material and that with it present no corrosion occurs even in cases where hydrochloric acid is present in the combustion gases. These acid bodies, as well as the esters and/or the neutral ketonic bodies aforesaid, appear to form a closely clinging and protective coating on the metal surfaces with the result that ordinarily considered corrosive vapors and/or gases do not act through the coating to cause corrosion of the metal. In cases where I make use of alkyl esters derived from the aforesaid acids, I may, and preferably do, first isolate the free acids content of the oxidation reaction mixture and esterify the so-isolated material using therefor saturated aliphatic alcohols such as methyl, ethyl, or like alcohol, as is more fully described, and claimed, in co-pending application Ser. No. 700,018, filed November 27, 1933, by Arthur W. Burwell and Adolf Kempe. Esterification of the total crude oxidation reaction mixture is open to the objection that it is less economical of the alcohol and involves handling of larger volumes of material.

Whatever their mode of preparation, I prefer that the top cylinder lubricant contain the aforesaid synthetic petroleum acid esters or the acids on which they are based in those cases where prevention of lead deposits and/or sulphate deposits (from sulphur or sulphur-containing compounds in the gasoline) in the combustion space of internal combustion engines is of particular moment, e. g., in the tetraethyl lead-containing gasoline used in high compression engines, particularly in airplane engines.

I have found that the said ester mixtures or acid-containing mixtures (for in each instance the lubricant aid is a mixture of a plurality of oxygenated compounds) are very readily saponified by lead oxide, being saponified when the oil compositions containing them come into contact with the aforesaid lead compounds. The resulting lead salt is soluble in petroleum oil, the major part of the top cylinder lubricant, and this latter has a higher relative affinity for metal surfaces than has the lead compound derived by combustion of tetraethyl lead, which circumstance apparently accounts for the fact that the said lead compounds do not stick to a surface which is bathed with the lubricant composition of the present invention. Whatever may be the scientific explanation therefor, it has been demonstrated in practice that by the use of the aforesaid esters and/or acid-containing mixtures in gasoline containing tetraethyl lead the mileages between engine overhauls are from two to three times as great as are possible using such gasoline in the absence of top cylinder lubricant. In these tests, made on airplane engines and also on automobile engines, it was found that the aforesaid compounds not only very considerably lessened the accumulation of lead compounds in the combustion space but also modified the physical as well as chemical character of the lead compounds. This latter was particularly noticeable in comparing the physical properties of lead deposits modified by the aforesaid compounds with those of lead deposits modified by the presence of dibrome-ethylene (an agent recently recommended for use in combating the lead deposits from gasoline containing tetraethyl lead). Where dibrom-ethylene is added to such gasoline and the gasoline is burned, halogen acid is set free, which acid may and frequently does, sufficiently escape reaction with the lead oxide to cause corrosion in the upper cylinder region (e. g., on valves and their seats, on the upper rings of the pistons, etc.). Moreover, the lead halogenides may and frequently do accumulate in the combustion chamber forming "crusts" or appreciable accretions which finally break loose from attachment to a surface and may be caught between a valve face and its seat thereby making possible the channelling of the valve and the reduction of that cylinder's efficiency. On the contrary, where the aforesaid synthetic compounds are employed as lubricant aids whatever lead deposit may accumulate is soft and readily deformable, making injury to the upper cylinder parts impossible.

In accordance with this latter embodiment of the invention I prefer to employ in the tetraethyl lead-containing gasoline an amount of my top cylinder lubricant such that the ester and/or acid content may be equivalent to the lead oxide calculatable from the tetraethyl lead content, together with sufficient lubricating oil to bring the total top cylinder lubricant to about 1%, more or less. While this represents the preferred proportion, it is to be noted that the relative content

of esters or acids may supply some reduction without complete loss of the improved effect.

In preparing the synthetic esters of the present invention the crude oxidation reaction mixture may be treated with aqueous saponifying agent (e. g., aqueous caustic soda) whereby two layers are formed: a supernatant oily layer and a subnatant aqueous layer containing the saponified acids. This latter layer is separated from the former, and the free acids liberated therefrom by treatment with an appropriate acid, e. g., sulphuric acid. The separated free acids may then be subjected to saponification treatment, by the process disclosed in application Serial No. 700,018 whereby there are formed the above-discussed saturated aliphatic esters of the acids. The esters are completely soluble in petroleum, have lower melting points than their corresponding free acids, and have a pleasant odor.

In making the lubricant aids of the present invention I prefer to employ oxygenated compounds of the types hereinbefore described, e. g., esters, of relatively low molecular weights, such as are obtained, through oxidation and appropriate after-treatment, of hydrocarbons in petroleum distillates of the order of 36–40 fuel oil distillate, 150 neutral oil, 200 neutral oil, etc. Such compounds are aliphatic chains having from 10 to 25 carbon atoms to the molecule. It should be noted that these low molecular weight oxygen-containing compounds (e. g., esters) have a more pronounced effect, per unit weight, in the present relations than do corresponding higher molecular weight compounds.

This application contains subject matter in common with my copending application serial No. 691,242, filed September 27, 1933, for "Top cylinder lubricants."

I claim:

1. A top cylinder lubricant and solvent composition for use in dissolving pitch deposits and lead deposits in, and lubricating and protecting surfaces of, a combustion chamber of an internal combustion engine, which comprises a solution, in a light hydrocarbon oil solvent of mineral origin including an oil having lubricating properties, of a mixture of saturated aliphatic oxygen-containing compounds of petroleum origin said compounds including alkyl esters, lactones, alcohol-ketones, ketones and alcohols, said oxygen-containing compounds being obtained by subjecting a petroleum hydrocarbon mixture to a liquid-phase partial oxidation treatment at an elevated temperature not exceeding 160° C. and at a superatmospheric pressure not exceeding 350 pounds per square inch and being contained in said solution in an amount, by volume equal to from about 3% to about 10% of the latter.

2. A top cylinder lubricant and solvent composition as defined in claim 1, characterized in that the light hydrocarbon oil solvent of mineral origin consists of a mixture of mineral seal oil and light lubricating oil each representing at least 25% of the solvent mixture.

3. A top cylinder lubricant and solvent composition as defined in claim 1, characterized by the following formula:

	Per cent
The oxygen-containing compounds	3
Mineral seal oil	25
Light lubricating oil	72

4. Composition for use in dissolving pitch deposits in, and lubricating surfaces of, a combustion chamber of an internal combustion engine, which comprises a solution of non-acidic, saturated, partially oxidized products of petroleum hydrocarbons in a mixture of a light hydrocarbon oil of low lubricating properties and a light hydrocarbon oil of mineral origin having lubricating properties, the latter being present in major amount, the oil of low lubricating properties being present in an intermediate amount and the non-acidic partially oxidized products being present in relatively very small amount.

5. Composition for use in dissolving pitch deposits in, and lubricating surfaces of, a combustion chamber of an internal combustion engine, which comprises a light hydrocarbon oil mixture of mineral origin containing dissolved therein a non-acidic mixture of aliphatic oxygen-containing compounds of petroleum origin, said compounds including alcohols, ketones, alcohol-ketones, lactones and esters, the composition having the approximate formula

	Per cent
Non-acidic mixture	3
Mineral seal oil	25
Light lubricating oil	72

6. A lubricated fuel for internal combustion engines, comprising gasoline containing dissolved therein a solution of non-acidic, saturated, partial oxidation products of petroleum hydrocarbons in a mixture of a light hydrocarbon oil of poor lubricating properties and a light hydrocarbon oil of mineral origin having lubricating properties, the said solution being additionally characterized in that the light hydrocarbon lubricating oil is present therein in major amount, the light hydrocarbon oil of poor lubricating properties is present in intermediate amount, and the non-acidic saturated partial oxidation products of petroleum hydrocarbons are present in very small amount.

ARTHUR W. BURWELL.