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LUBRICATING OILS

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This invention relates to improved lubricating oils, and more particularly to lubricating oils containing a mixture of oil from crude petroleum and of synthetic oil. The oils so prepared are especially suited for the lubrication of internal combustion engines in heavy duty service.

In the progressive improvement in design of internal combustion engines, particularly with respect to performance and efficiency, the temperatures and pressures prevailing in the various parts of the engines have been gradually increasing. Higher efficiencies are being obtained through increase in pressure in the cylinders with corresponding increase in temperature in the combustion region. Increase in power without increase in engine weight is being obtained in part through increase in engine speed, with accompanying higher temperatures. In addition to these design factors, there is a trend in the utilization of internal combustion engines to use greater proportions of the maximum available power for prolonged periods of operation, thereby increasing the severity of operating conditions, especially engine temperatures.

Particularly, in aircraft and high speed Diesel engines, and in some cases in automotive engines, the maximum engine power output or the period of satisfactory operation of the engine is limited by the accumulation of deposits in various parts of the engine.

The deposits found in internal combustion engines result from the influence of a number of factors and through a wide variety of chemical sequences. Oxidation of oil through the effects of heat, air, combustion gases, metal catalysts, etc., forming both direct oxidation products and products which are the result of oxidation together with polymerization, condensation, etc., constitutes one of the major sources of deposits. This invention is not concerned with the formation of such oxidation products, which are controlled primarily through oil refining methods and through the use of various type of antioxidants.

Thermal decomposition or cracking of lubricating oils also results in the formation of objectionable residues in internal combustion engines. The oil which lubricates the cylinder walls of internal combustion engines is exposed directly to the combustion flame. The heads or tops of the pistons and frequently the piston ring regions attain temperatures in the cracking range of petroleum oils. Piston crown and top land temperatures above 600° F. are frequently found, and temperatures of 700 and 800° F. are not uncommon. In many of the recent engine designs oil streams are directed to the regions of high temperatures as a cooling medium. The valves and valve stems also become heated to oil cracking temperatures; the exhaust valves especially attain high temperatures through direct contact with the hot combustion gases. These products of decomposition which remain in the engine are usually hard carbonaceous residues, producing malfunctioning of piston rings and valves through their hindrance of normal movements. Through the abrasive nature of some types of residues, the pistons, cylinders, valve stems, and valve guides may become scratched and roughened, thereby greatly reducing the efficiency of the engine.

It is an object of this invention to disclose and provide lubricating oils which form substantially no residues as a result of thermal decomposition.

It is a further object of this invention to provide a more suitable oil for the lubrication of internal combustion engines, particularly those in which high internal temperatures are encountered.

It is a further object of this invention to disclose a method of preparation of lubricating oils which substantially eliminate the formation of deposits resulting from thermal decomposition of the oils.

It is a further object of this invention to disclose a method of preparation of lubricants forming substantially no residue on thermal decomposition through the blending of appropriate oils from crude petroleum and synthetically prepared products.

It is a further purpose of this invention to disclose a method of utilizing selected portions of refined crude oils and of synthetic oils for the preparation of lubricants which form substantially no residues on decomposition.

Other objects of this invention will become apparent to one skilled in the art from the accompanying disclosure and discussion.

I have discovered that lubricating oils of superior qualities, especially freedom from deposits resulting from decomposition, may be produced by the combination of lower viscosity oils which have been segregated from crude petroleum, or other similar sources, together with higher viscosity oils which have been prepared synthetically. The exact ranges of viscosity of these two types of oils for a particular use depend upon the range of molecular weight, viscosity, or distilling characteristics of the oil from crude petroleum, the type of crude, and the refining of the oil, and upon the physical properties as well as the viscosity range of the synthetic oil, as more fully discussed herein.

In the manufacture of lubricating oils, it has become the practice to select as starting material a crude petroleum fraction, usually a residue remaining after removal of the lower boiling components, which contains a relatively large proportion of paraffinic or non-cyclic hydrocarbon structures, and to utilize refining methods which will selectively remove the less paraffinic components. These preferred hydrocarbon oils are characterized by high viscosity index values, high distillation temperatures, high hydrogen to carbon ratios, and the formation of relatively low proportions of insoluble products on oxidation.

When oils of this general type are subjected to temperatures sufficiently high to produce thermal decomposition, usually in excess of 650 or 700° F., vaporization or thermal decomposition of the oils may occur, depending upon the molecular weight or distillation range of oil. The vapor pressures of the paraffinic oils having viscosities in the range of 100 to 350 seconds Saybolt, or thereabouts, at 100° F. are sufficiently high that at decomposition temperatures the oils vaporize under conditions normally prevailing in internal combustion engines, so that little or no carbonaceous deposits result. On the other hand, the more viscous oils, especially those which are prepared as residual stocks, have such high boiling temperatures that their vapor pressures are inadequate to permit vaporization without decomposition, with the result that thermal decomposition with accompanying deposition of coke and carbonaceous residues result when the oil becomes heated to a sufficiently high temperature. The change in mean boiling temperatures (determined under subatmospheric pressures and corrected to atmospheric pressure) with change in viscosity grade for relatively closely cut fractions of a typical paraffinic oil prepared from a Mid-Continent crude oil are shown in Table I.

Table I

SAE viscosity numbers	Mean boiling temperature
	°F
10	810
20	850
30	890
40	920
50	960
60	1,000

The SAE viscosity numbers constitute a recognized classification of crankcase lubricating oils in terms of viscosity. The viscosity values represented by the numbers are recorded in the handbook of the Society of Automotive Engineers. The transition from oils which vaporize without the formation of deposits to higher molecular weight oils which are insufficiently volatile to prevent coke formation at decomposition temperatures is a very gradual change, so that specification of a maximum boiling temperature or viscosity grade is not possible. The tendency for deposition of carbonaceous deposits is also dependent on engine design and service factors.

The residual type oils, or those containing relatively non-volatile components, have been found undesirable for use in some engines under heavy duty conditions on account of the formation of residues. It has similarly been found that blends of the lower viscosity oils usually produced by distillation, so-called neutral oils, with the residual type oils or bright stocks, are also sources of deposits through thermal decomposition. Since blending of the lower and higher viscosity oils is the conventional method for obtaining the various viscosity grades commercially required, the formation of deposits from such oils in engines under high output conditions imposes a limitation on the type of oil used in the engine or on the severity of conditions under which the engine may be operated.

In contrast to the lubricating oils prepared from crude petroleum the oils or blending stocks in the viscosity range of lubricating oils prepared by the polymerization of olefins decompose without the formation or deposition of carbonaceous matter or coke when subjected to sufficiently high temperatures. The polymeric compounds decompose with the formation only of volatile molecular fragments, usually similar in molecular size to the original monomeric materials, or multiples of them. The difference in behavior of the natural and synthetic oils is believed to result from the presence of secondary and tertiary carbon bonds in the chain structure of polymers, in contrast to the primary bond structure of the naturally occurring oils.

The olefins used as charge stocks for the manufacture of synthetic lubricating oil stocks may include the lower molecular weight olefins such as propylene, the butenes, and the like, or higher molecular weight olefins, even those derived from waxy hydrocarbons by dehydrogenation processes, etc. The preferred catalysts for the conversion of these olefins to polymers in the lubricating oil range include the Friedel-Crafts type catalysts such as aluminum chloride, boron fluoride, and zirconium tetrachloride, and the like and also hydrogen fluoride and the like. Polymers in the suitable viscosity range may be used directly as lubricants, but to improve the resistance of the polymers to oxidation and chemical change, it is usually desirable to hydrogenate the olefinic polymer non-destructively. In some cases, especially when superior solvent characteristics are desired, the olefinic polymer may be joined with aromatic, cycloparaffinic, alcoholic, or other groups by suitable reactions. Such synthetic oils are the ones I particularly prefer to use in the practice of the present invention. Synthetic oils prepared by other methods which meet satisfactorily the requirements of the invention, such as some substantially paraffinic products of destructive hydrogenation, may also be used, although they are not to be considered as equivalents.

In such polymerization systems, when high yields of satisfactory oils are obtained, it is usually found that the proportion of low viscosity oils, 100 to 350 seconds Saybolt viscosity at 100° F., is low, whereas the proportion of more viscous oils is usually quite high.

In numerous internal combustion engines lubricated with a variety of synthetic oils prepared as previously indicated, it was observed that practically no carbonaceous deposits were found in the regions of high temperature in the engines. Even under the severe conditions which rapidly caused deposition of carbonaceous residues in upper piston regions and on valve stems with lubricants containing residual type oils from crude petroleum, no deposits were found in engines similarly operated with a synthetic

oil blend containing a fraction having a viscosity of 230 seconds Saybolt at 210° F.

One limitation in the utilization of synthetic oils of lower viscosity results from the relatively high volatility, or low boiling points, of the synthetic oils, especially those prepared from the lower molecular weight olefins. In engines lubricated with a relatively narrow boiling fraction of synthetic oil in the SAE 20 viscosity range, the consumption of oil was approximately 3 times that found in lubricating the same engines with a narrow boiling fraction of similar viscosity prepared from crude petroleum. These differences in volatility or boiling temperatures are evident on comparing the mean boiling temperatures of various narrow boiling fractions of various hydrogenated olefin polymers of similar viscosity which are shown in Table II, with those previously reported for oil fractions prepared from crude petroleum. It is also evident from these data that the boiling temperatures of the oils of SAE 50 viscosity number or higher, or of 100 seconds Saybolt viscosity at 210° F. or higher, are sufficiently high that relatively little loss through vaporization takes place.

Table II

SAE viscosity number	Mean boiling temperature, °F.			
	Hydrogenated isobutylene polymer	Hydrogenated propylene polymer	Hydrogenated pentene-1 polymer	Natural paraffin oil
10	662	694	765	810
20	694	729	801	850
30	723	759	835	890
40	756	792	867	920
50	799	835	910	960
60	830	864	946	1,000

I have now found that lubricating oils of desirable viscosity characteristics which produce substantially no nonvolatile, gummy, tarry, coke-like, or lacquer-like residues either in laboratory tests or during actual operation, may be produced by blending natural oils of low viscosity and synthetic oils of higher viscosity, each in substantial amounts. In the general practice of my invention, the blends will be formed to meet the usual SAE viscosity number specifications, although any other standard, or specification, may be met. The relative amounts of each constituent in the final blend will depend on the characteristics of the desired blend and on the characteristics of each of the components, however, each of the constituents will have viscosities similar to usual blending stocks, that is, they will be in the lubricating oil viscosity range. More than one natural or synthetic stock may be used, but generally only one of each will be necessary. Most of the blends which will be prepared in accordance with the present disclosure will include at least about 10 per cent of the synthetic oil stock, and amounts in excess of about 90 per cent will generally not be practical. I prefer to use natural oils which have viscosities in the range of about 100 to about 350 seconds Saybolt viscosity at 100° F., although some natural oils as viscous as about 600 seconds at 100° F. may be used in particular blends. In any case, the natural oils should be capable of vaporizing under atmospheric pressure, substantially completely below the temperature at which they undergo extensive cracking or coke formation. Such natural oils will have viscosities of about 35 to about 55 to 70 seconds Saybolt viscosity at 210° F. The natural oil will generally have been subjected to, or will have resulted from, one or more of the usual refining procedures, including distillation, dewaxing, solvent extraction, and the like, as will be appreciated by one skilled in the art. The synthetic oil should be more viscous than the natural oil with which it is blended, and I prefer to use synthetic oils having viscosities in the range of about 80 to about 200 seconds Saybolt viscosity at 210° F., although some synthetic oils as viscous as about 500 seconds at 210° F. may be used in a particular instance. As brought out by the data just cited, the synthetic oils have lower mean boiling temperatures, or higher volatilities, than natural oils of similar viscosity characteristics. Other known methods of evaluating the volatility of a lubricating oil is a determination of its flash and/or fire point, lower values indicating higher volatilities. In blending two or more lubricating oil stocks, the volatility characteristics of the blend are found to be more or less directly proportional to the volatility characteristics and amount of each blending stock. In practicing my invention, therefore, care should be exercised not to use so much of a synthetic oil of high volatility as to produce a blend which will have a volatility high enough to result in high loss during subsequent use. In preparing the more viscous blends this will be of less importance than with less viscous blends, as the more viscous synthetic oils have low volatilities, comparatively. In general, the volatility of the synthetic oil should not be materially, if any, greater than that of the natural oil with which it is blended.

It has previously been proposed to use extremely viscous synthetic oils to improve viscosity index characteristics of lubricating oils, such synthetic oils having molecular weights of about 1,000 to 10,000, or more. It will be appreciated that the synthetic oils used in this invention are not of this nature, although such very viscous materials may be incorporated in a blend prepared according to the present invention.

The Conradson carbon residue test has been recognized as a means of indicating the relative carbon-forming propensity of an oil. The method has been standardized by the American Society for Testing Materials, for example. The differences in carbon-forming characteristics of oils prepared from crude petroleum, and from blends of relatively low viscosity oils from crude petroleum and relatively high viscosity synthetic oils, in accordance with the present disclosure, are indicated by the test results shown in Table III.

Table III

Constituents of blend	Composition of blend				
(a) Refined fraction from crude petroleum 180 seconds Saybolt viscosity at 100° F.	0	7	7	0	10
(b) Refined residual product from crude petroleum 170 seconds Saybolt viscosity at 210° F.	10	3	0	0	0
(c) Synthetic oil from polymerization of low boiling olefins and hydrogenation of polymer 220 seconds Saybolt viscosity at 210° F.	0	0	3	10	0
Conradson carbon residue, per cent	1.39	0.45	0.01	0.01	0.02

Similar results have been obtained in a supercharged gasoline engine. Using as lubricant an oil having a viscosity of 90 seconds Saybolt viscosity at 210° F., (SAE viscosity number 50) which contained 70 per cent of a residual type oil from crude petroleum having a viscosity of 120 seconds Saybolt at 210° F., and 30 per cent of

a neutral oil from a similar source, after 50 hours operation there was found 23.5 grams of carbon on the piston lands and in the ring grooves. When a lubricant of 94 seconds Saybolt viscosity at 210° F. (SAE viscosity number 50) which was prepared from a neutral oil from crude petroleum having a viscosity of 170 seconds Saybolt at 100° F. and from a narrow boiling fraction of a synthetic oil, prepared by the polymerization of low-boiling olefins and hydrogenation of the polymer, and having a viscosity of 180 seconds Saybolt at 210° F. had been used in the same engine under similar conditions, only 1.4 grams of carbon was found in the piston ring region. The marked decrease in amount of coke and carbonaceous material formed which resulted from the substitution of the viscous synthetic oil in the blend of oils was very evident on visual inspection. In general, oils prepared in accordance with this invention will have Conradson carbon residue values less than 0.05 per cent, and even for blends of the highest viscosity this value will be less than about 0.1 per cent. In most cases, this value will be only about 0.01 to 0.02 per cent.

The oils prepared by blending lower viscosity neutral oils from crude petroleum with higher viscosity synthetic oils are found to be deficient in resistance to oxidation, to catalytic effects of metals, etc. These qualities may be greatly improved through the addition of specific types of inhibitors as known in the art. In a particular instance, a combination of 0.5 per cent alkylated phenol, 1.0 per cent of an aliphatic sulfur compound, and 0.3 per cent of a tin derivative of a complex phenolic compound was found to markedly increase the stability of the oil used in an engine under severe operating conditions, and more importantly permitted operation of the engine for prolonged periods without the accumulation of deposits. The addition of chemically active materials to these new oils for particular purposes will in many cases be desirable, with the exact combination of active materials depending upon the requirements of the particular service in which the oil is to be used.

The advantages in various use of oils which form substantially no non-volatile products on thermal decomposition, and which have volatility characteristics comparable to those of oils from paraffinic type crude petroleums are readily appreciated by those skilled in the art, and various modifications of my invention may be practiced without departing from the scope or spirit of the teachings of this disclosure.

I claim:

1. A lubricating oil blend of SAE 50 viscosity number having a low vaporization loss in use and a low carbon deposition in use and comprising a neutral oil from crude petroleum having a narrow boiling range and a viscosity of 170 seconds Saybolt at 100° F. and a hydrogenated olefin polymer oil having a narrow boiling range and a viscosity of 180 seconds Saybolt at 210° F., said blend having a Conradson carbon residue not greater than 0.02 per cent.

2. A lubricating oil blend in the range of SAE 40 to SAE 60, having a low vaporization loss in use and a low carbon deposition in use and comprising a neutral oil from crude petroleum having a narrow boiling range and a viscosity in the range of about 100 to about 350 seconds Saybolt viscosity at 100° F. and not greater than 55 seconds Saybolt at 210° F., in an amount in the range of 10 to 90 per cent, and as the remainder an oil, prepared from an olefin polymer, having a narrow boiling range and a viscosity in the range of about 80 to about 200 seconds Saybolt viscosity at 210° F., said blend having a Conradson carbon residue not greater than 0.02 per cent.

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