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LUBRICANT FOR INTERNAL COMBUSTION ENGINES

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My invention relates to improved lubricants for use in internal combustion engines, such as automotive engines, aviation engines and Diesel-type engines, and in particular to a lubricant comprising a major amount of a petroleum lubricating oil, having incorporated therein small amounts of nickel naphthenate and a certain type of alkylated phenol, having anti-oxidant properties.

Progress in the design of internal combustion engines of all kinds tends to impose more and more severe burdens upon lubricants employed therein. The general tendency is always in the direction of higher performance and increased horse power per unit of weight. This tends to make lubrication more difficult and frequently to introduce entirely new problems into the preparation and selection of lubricants for a particular engine or type of engine. Individual lubricating problems arise with reference to different points in the engine. A satisfactory solution of any one of these individual problems alone is sometimes difficult enough in itself but becomes further complicated when, as is frequently the case, it is found that improvement of a lubricant with respect to one problem may make another problem in the same engine more serious.

Thus, it has been found that a lubricant giving generally good "crankcase performance" in a particular engine may not be entirely satisfactory for lubrication of the cylinder walls, piston and piston rings of the same engine, and vice versa. That is because entirely different physical conditions are encountered in the cylinder than are encountered in the crankcase. Temperatures, rubbing speeds, unit pressures, and other factors vary considerably at different points in any internal combustion engine. Nevertheless the design of internal combustion engines is such that a single lubricant is required, and that lubricant must give satisfactory service under the variety of conditions encountered in each engine.

To illustrate this more fully, a good crankcase lubricant should be as free as possible from sludging tendencies, and its viscosity change in a given temperature variation should be a minimum, i. e., it should have a high viscosity index. Paraffinic petroleum oils, such as those obtained from Pennsylvania crudes, possess these characteristics to a greater extent than do lubricating oils made by ordinary refining methods from less highly paraffinic crudes, such as Coastal and Mid-Continent crudes. During the past decade or so, great strides have been made in refining methods, so that it is now possible to produce from the less highly paraffinic crudes lubricating oils which approach Pennsylvania lubricating oils in general performance characteristics. Even Pennsylvania oils are refined to increase their purity and paraffinicity. One of the best general automotive lubricants in use today is made from Pennsylvania crude stock, drastically refined by means of aluminum chloride; the resultant lubricant oil, without any synthetic additions, is approached in value only by some oils which have been carefully refined and then improved by the addition of various and more or less synthetic improvement agents.

In any event, the general crankcase performance of such oils is excellent and they command a justified premium on that account.

Nevertheless, as might be expected, the fact that these oils possess excellent crankcase performance characteristics does not mean that these oils are not susceptible to improvement with respect to performance under special conditions and at particular points in internal combustion engines where the conditions are radically different from those encountered in the crankcase. Moreover, in improving such highly refined oils, with respect to their performance characteristics under such particular conditions problems are sometimes encountered which, for various reasons, are more difficult to solve than would be true of less highly refined oils.

That has been true, for example, with respect to corrosion of certain types of corrosion-sensitive metal bearing alloys such as the well known "cadmium-silver," "copper-lead," and "cadmium-nickel" bearing alloys. In proper engine designs these bearings should give little or no trouble with any oil, but in occasional instances the design of the engine may be such (particularly where excessive bearing temperatures are maintained) that we are confronted with the apparent paradox that the "best" oils do not give the best over-all results and may even be undesirable under particular conditions. It is generally known that the more highly refined oils are, for some reason, occasionally more likely to cause more corrosion of sensitive alloy bearings at high temperatures than is true of the less highly refined oils.

It might at first be thought that the simple remedy would be to reduce the degree of refining and to go back to cheaper oils. That can be done, however, only by sacrificing general crankcase performance characteristics of the

highly refined oils, which is undesirable. And it has been found that this particular problem can be met satisfactorily and without such a sacrifice by the use of small quantities of addition agents having a specific and beneficial effect upon the particular problem referred to but which do not impair the primary physical characteristics and the general performance characteristics of the lubricant and, obviously, that is the way the problem should be solved.

My invention is concerned, however, not with corrosion problems alone, but also with the problems encountered in upper cylinder lubrication of internal combustion engines. The difficulties encountered in the cylinders manifest themselves more apparently, from the standpoint of the user, in what is generally known as "ring-sticking." No internal combustion engines of the ordinary type are entirely free from this tendency, but it is encountered more frequently and more seriously in connection with heavy duty engines, such as Diesel-type and aviation engines. The disadvantages of a lubricant which tends to cause the piston rings to become stuck are too obvious to require discussion. Suffice it to say that a satisfactory lubricant should permit an engine to run at high speed with high load for a long period of time without any appreciable ring-sticking tendency other than that attributable to mechanical features of the engine design rather than to any failure on the part of the lubricant.

The problem of ring-sticking is extraordinarily complex. That this would necessarily be the case is evident from the fact that combustion is taking place at or adjacent to the points requiring lubrication. Temperatures tend to be very high, and there is a pronounced tendency for the lubricating oil to be burned or oxidized or otherwise removed from the metallic surfaces in moving contact with each other. Years will probably pass and much intensive research will be done before those in the art are able to specify with any degree of certainty the fundamental cause or causes underlying the "ring-sticking" tendencies and characteristics of petroleum lubricants.

It has been observed that ring-sticking is usually accompanied by the accretion of more or less solid deposits around the rings and on the adjacent metal surfaces being lubricated. These deposits may take the form of carbon, or heavy hydrocarbons (generally referred to as "gum," although not necessarily analogous to the gums formed in cracked gasoline distillates), or they may appear as lacquer-like deposits. These three types of deposits result from various types of chemical actions and are not necessarily interrelated except for the fact that they are solid in character; for that reason their accretion tends to prevent or interfere with normal action of the piston rings. No oils are entirely free from these tendencies, but some oils, for no readily apparent reason, are better than others, and oils which may produce generally equivalent results may actually do so through the mechanism of entirely different chemical reactions.

Thus it has been observed that in the operation of Diesel engines, using lubricants derived from Coastal crudes, ring-sticking tendencies tend to show up more rapidly and more seriously with respect to the bottom piston rings of a particular engine, whereas there is a tendency for the top rings to stick first when the same engine is lubricated with paraffin base oils. It would appear that the phenomenon is not only connected with temperature but also with the chemical composition of the oil.

On the other hand, a lubricating oil which tends to undergo excessive sludging in the crankcase may give excellent performance characteristics with respect to ring-sticking. Such an oil, even when employed in a heavy-duty Diesel engine, may leave the piston ring assemblages relatively clean and clear. A better oil, however, should give good over-all performance characteristics. It should not be necessary to sacrifice desirable crankcase performance characteristics in order to achieve freedom from ring-sticking and the deposition of gum and lacquer in the upper cylinders.

It appears, in general, that the deposition of gum in the cylinders is related in some manner to the volatility of the lubricating oil, and that as between two oils of the same viscosity, one of which is a straight distillate (particularly one having a low end boiling point) and the other is a residual oil or a blend containing a residual oil, the latter will be found to cause more gum formation and hence more ring-sticking than will be true of the former. It is not, however, possible to overcome the problem fully by simply employing a distillate oil or selecting an oil of a given volatility.

Others have suggested, prior to my invention, that certain metallic soaps will stabilize petroleum lubricating oils against oxidation, polymerization or a combination thereof, which would ordinarily tend to result in the deposition of carbonaceous material or sludge and in an undesirable change of color. The naphthenates of manganese, cobalt, lead and zinc have all been suggested as antioxidants for lubricating oils. Whether or not such naphthenates are actually effective antioxidants under conditions of use in internal combustion engines is, however, not a simple question to answer. The action of naphthenates in preventing or promoting oxidation appears to be a function of temperature to a very considerable extent. At atmospheric temperatures an antioxidant effect may be observed, resulting in a decrease in the tendency of the compounded oil to form sludge on oxidation. At somewhat higher temperatures, however, metallic naphthenates such as copper naphthenate may have exactly the opposite effect. It has been found, for example, that copper naphthenate will actually increase sludge formation at a temperature of 310° F. when compounded with a well known Pennsylvania motor oil of SAE 20 grade. At still higher temperatures, of say from 350° to 600° F. or even higher, naphthenates tend to exert a pro-oxidant effect on petroleum oils, so strong as to cause the oil to oxidize fairly completely and leave a minimum of residue.

Since these metallic naphthenates in general do have such a pro-oxidant effect, it has been suggested that certain naphthenates, such as aluminum naphthenate and calcium naphthenate be used as anti-ring-sticking agents for lubricants, especially lubricants intended for use in Diesel and other heavy duty internal combustion engines.

In a copending application filed concurrently herewith, Toussaint, Gaspari and Ambrose state that they have found, however, that nickel naphthenate is exceptionally useful and advantageous, when incorporated in petroleum lubricating oils intended for use in internal combustion engines in improving the upper cylinder performance characteristics and ring-sticking behavior of the

oil, without on the other hand promoting oxidation under the conditions normally obtained in the crankcase of internal combustion engines.

Not only have Toussaint et al. found that far smaller amounts of nickel naphthenate are necessary for incorporation in lubricating oils in order to give a desired degree of improvement than is true of other naphthenates, but they have also found that nickel naphthenate is effective in producing improvement of certain highly refined oils of the character set forth hereinabove, the upper cylinder performance characteristics and ring-sticking tendencies of which are not substantially improved by the incorporation therein of other naphthenates, such as aluminum naphthenate.

The aforesaid invention of Toussaint et al. represents a valuable contribution to the art. It deals, however, primarily with the problem of preventing ring-sticking and is not concerned with the problem of lubricating corrosion-sensitive metal bearing alloys, such as alloys of the "cadmium-silver" and analogous types, especially at high temperatures.

When it is attempted to solve both of these problems simultaneously, unforeseen difficulties arise. It has been found, for example, that some addition agents which are effective with respect to the solution of one of these problems may have an adverse effect with respect to the other. Thus certain oil-soluble phosphorus esters have been proposed as agents for preventing corrosion of sensitive metal bearing alloys, when incorporated in petroleum lubricants. Some of these phosphorus esters have been found, however, to promote the formation of lacquer-like deposits from oils containing them. These phosphorus esters are also subject to certain other disadvantages; in particular, many of these esters are unstable in the presence of moisture and some are unstable under the high-temperature conditions prevailing in the upper portions of the cylinders of internal combustion engines.

Moreover in making any lubricant composition containing two or more addition agents of distinct chemical types, careful selection and testing are necessary in order to insure that undesirable products will not be formed as a result of reactions between the individual agents employed. Consideration must be given not only to the possibility of reaction under ordinary atmospheric conditions, but also at the high temperatures prevailing at various points in the engines to be lubricated.

As aforesaid, there is a definite possibility that nickel naphthenate acts to prevent ring-sticking by virtue of a pro-oxidant effect rather than because of any anti-oxidant effect. In other words, this compound tends to cause the oil to oxidize very rapidly, thereby leaving a minimum of residue. Consequently, it would be expected that the presence of an anti-oxidant would be detrimental.

I have found, however, that petroleum lubricating oils containing small amounts of both nickel naphthenate and a certain type of antioxidant are surprisingly free from corrosion and ring-sticking tendencies and my invention therefore comprehends lubricants, especially adapted for use in internal combustion engines, containing small amounts of both of these addition agents.

The antioxidants to which I refer comprise in general certain oil-soluble alkylated phenols. These are condensation products of low-boiling olefins and monohydric phenols, and comprise alkylated monohydric phenols having at least one alkyl group in a position ortho to the hydroxyl group and at least 4 carbon atoms in the alkyl groups in the positions ortho to the hydroxyl group. Included within this classification are certain tertiary butyl phenols, such as 2,6-di-tertiary-butyl-4-methyl phenol and 2,4,6-tri-tertiary-butyl phenol, as well as corresponding tertiary amyl phenols. These alkylated phenols are powerful antioxidants and possess an advantage in that they are insoluble in water and in dilute aqueous alkaline solutions. While various members of the group indicated are useful, I have found that 2,6-di-tertiary-butyl-4-methyl phenol is by far the most effective for the purposes of my present invention.

Thus I have found that a given petroleum oil having highly desirable general crankcase performance characteristics is nevertheless susceptible of improvement, both with respect to its tendency to produce corrosion of corrosion-sensitive alloy bearings at high temperatures and with respect to its tendency to promote ring-sticking in heavy duty engines of the Diesel type. The addition of nickel naphthenate alone to this oil decreases the tendency of the oil to cause ring-sticking, as has been pointed out by Toussaint et al., but gives no improvement with respect to the corrosion of corrosion-sensitive bearings, such as "cadmium-silver" alloy bearings.

On the other hand, the addition to the same oil of a small quantity of the preferred alkylated phenol mentioned above materially decreases the tendency of the oil to cause corrosion of corrosion-sensitive bearings, but is not especially effective in promoting freedom from ring-sticking tendencies.

However, when small amounts of nickel naphthenate and the preferred alkylated phenol referred to are added in admixture to the same oil, I have found, surprisingly enough, that the compounded oil is markedly superior to either of the compounded oils referred to hereinabove, with respect to both bearing corrosion and ring-sticking tendencies.

By way of comparison with these results, it may be added that when an equivalent amount of aluminum naphthenate is substituted for the amount of nickel naphthenate employed (the amount of alkylated phenol remaining the same), the compounded oil is inferior, with respect to bearing corrosion, to the composition containing the alkylated phenol alone, and is no better with respect to ring-sticking than the uncompounded oil.

These results could not possibly have been predicted from a consideration of the individual effects of naphthenates and alkylated phenols when employed alone.

Therefore my invention comprehends the improvement of petroleum lubricating oil, especially for use in internal combustion engines, by incorporating therein relatively small amounts of nickel naphthenate and 2,6-di-tertiary-butyl-4-methyl phenol or other alkylated phenol of the character indicated above.

In preparing the improved lubricating composition of my invention various petroleum oils may be used; the selection of the particular oil base is largely dependent upon the type of service intended. Various petroleum lubricating oils, preferably of the well known SAE grades, may be employed. The preferred oil bases, however, are the more refined and highly paraffinic oils, the best being an aluminum-chloride-refined oil obtained from Pennsylvania crude stock. Oils ob-

tained from Coastal and Mid-Continent crudes may also be employed although, contrary to the experience of the art, Coastal oils (when compounded in accordance with my invention) are inferior to highly refined Pennsylvania oils similarly compounded, for use in Diesel-type engines.

Similarly, the amounts of the individual addition agents employed will vary in accordance with the character of the oil, the results desired, and the severity of service conditions likely to be encountered. Ordinarily, it is desirable to incorporate each of the two addition agents in the oil in an amount representing from 0.05 to 2.0 per cent by weight of the respective agent, based on the lubricating oil. I have obtained excellent results with oil compositions containing 0.2 per cent of nickel naphthenate and 0.2 per cent of 2,6-di-tertiary-butyl-4-methyl phenol, and also with compositions in which the amounts of the individual ingredients range from 0.1 to 0.6 per cent, which is the preferred range in most cases.

I have subjected oils compounded in accordance with my invention to an extended series of tests commonly employed by experts in the art for evaluating lubricants intended for use in internal combustion engines. The results have been uniformly satisfactory. Under these tests my improved compositions showed remarkable freedom from ring-sticking and "blow-by" tendencies and also remarkable freedom from tendencies to deposit sludge, carbon, lacquer or gum in the ring grooves and on the piston surfaces of internal combustion engines. They do not cause corrosion of "cadmium-silver" and like bearing metal alloys. Moreover, the characteristics of the used oils, after testing, are superior to those of lubricants otherwise compounded, of which I have tested a large number.

Moreover, so far as I am aware, oils compounded in accordance with my invention do not possess any disadvantages, or at least do not possess any disadvantages such as would be brought out by careful consideration of the results obtained in engine and other tests actually performed.

While I have described my invention hereinabove with respect to various specific details and embodiments and particularly with reference to a preferred specific embodiment, it will be understood by those skilled in the art that my invention in its broadest aspect is not limited to such details, but may be variously praticed and embodied within the scope of the appended claims.

What I claim is:

1. A lubricating composition, for use in internal combustion engines and the like, comprising a major amount of a mineral lubricating oil having incorporated therein small amounts, not in excess of 2 per cent by weight of the oil, of nickel naphthenate and an alkylated monohydric phenol having at least one alkyl group in a position ortho to the hydroxyl group and at least 4 carbon atoms in the alkyl groups in positions ortho to the hydroxyl group.

2. A lubricating composition, for use in internal combustion engines and the like, comprising a major amount of a mineral lubricating oil having incorporated therein small amounts, not in excess of 2 per cent by weight of the oil, of nickel naphthenate and 2,6-di-tertiary-butyl-4-methyl phenol, respectively.

3. A lubricating composition, for use in internal combustion engines and the like, comprising a major amount of a mineral lubricating oil having incorporated therein small amounts, not in excess of 2 per cent by weight of the oil, of nickel naphthenate and 2,4,6-tri-tertiary-butyl phenol, respectively.

4. A lubricating composition, for use in internal combustion engines and the like, comprising a major amount of a mineral lubricating oil having incorporated therein small amounts, not in excess of 2 per cent by weight of the oil, of nickel naphthenate and 2,6-di-tertiary-amyl-4-methyl penol, respectively.

5. A lubricating composition, for use in internal combustion engines and the like, comprising a major amount of a mineral lubricating oil having incorporated therein from 0.05 to 2.0 per cent by weight of nickel naphthenate and from 0.05 to 2.0 per cent by weight of 2,6-di-tertiary-butyl-4-methyl phenol.

6. A lubricating composition, for use in internal combustion engines and the like, comprising a major amount of an aluminum-chloride-refined, Pennsylvania-base, petroleum lubricating oil having incorporated therein approximately 0.2 per cent by weight of nickel naphthenate and approximately 0.2 per cent by weight of 2,6-di-tertiary-butyl-4-methyl phenol.

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