Patented June 12, 1945 2,377,909

UNITED STATES PATENT OFFICE

2,377,909

LUBRICATING OIL COMPOSITIONS

Paul R. Van Ess, Berkeley, and Ellis R. White, Albany, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application December 26, 1941, Serial No. 424,545

7 Claims. (Cl. 252—53)

This application is a continuation-in-part of our copending application Serial No. 376,330, filed January 28, 1941.

The invention relates to compounded lubricating oils containing added ingredients which improve their properties in one or more important respects. It also deals with the addition of oil-soluble addition agents to compounded mineral oils to produce lubricating oils of improved anti-wear properties for internal combustion engines. More particularly, it deals with the addition to lubricating oils of certain oil-soluble carbocyclic compounds, which compounds have the property of modifying or reducing the hardness of carbon formed on pistons and of preventing the baking of carbon in piston grooves to the point of hardness and thus not only retarding the sticking of piston rings when running internal combustion engines for long periods of time, but also preventing the scratching of pistons caused by hard carbon.

It is known that in modern internal combustion engines, such as aviation gasoline engines, due to their high power output and their relatively high temperatures, or high speed Diesel engines, due to incomplete combustion of the fuel, piston rings have a tendency to become stuck in the grooves due to baked carbon, and the pistons tend to become worn. Baked carbon on pistons lubricated with hydrocarbon oils, in general, may be said to increase in hardness and decrease in adhesiveness with rise in viscosity index of the oil.

We have discovered that certain oil-soluble saturated alicyclic alcohols or esters thereof are useful in modifying hard carbon; and that highly-refined lubricating oils which contain small amounts of such compounds are remarkably stable and have the valuable property of positively retarding ring-sticking, and overcoming and preventing piston scuffing and scratching usually associated with the severe service conditions such as are encountered in Diesel engines and the like.

In stating that the cyclic alcohols or esters modify the carbon formation on the piston, we mean that instead of the usual hard, tough adhesive carbon deposits, a soft, velvety, non-adherent carbon deposit is formed in the presence of the cyclic alcohols or their esters, which deposit is almost oily in character. It is so non-adherent that it may be removed by wiping with a soft cloth, leaving a clean metal surface. No explanation can be offered for the above-observed phenomenon.

The cyclic alcohols or esters possessing carbon-modifying properties may be represented by the general formula

$$R-(X)_n$$

wherein R represents a high-molecular weight saturated hydrocarbon radical having at least 12 carbon atoms and containing at least one alicarbocyclic ring, X represents a hydroxy or ester radical attached to a nuclear carbon of said alicarbocyclic ring, and n is an integer, preferably having the value 1.

Saturated alicyclic alcohols of at least 12 carbon atoms useful for our purpose may be mononuclear, monohydroxy alcohols of at least 12 carbon atoms, such as straight and branched chain alkyl cyclopentanols, e. g., tri-n-propyl, tri-isopropyl, di-primary, secondary or tertiary butyl, dimethyl amyl, methyl hexyl, ethyl hexyl, dimethyl hexyl, heptyl, methyl heptyl, diheptyl, octyl, isooctyl, etc., cyclopentanols; normal and branched alkyl cyclohexanol, e. g., di-isopropyl cyclohexanol, di-n-amyl cyclohexanol, di-secondary-amyl cyclohexanol, di-tertiary amyl cyclohexanol, n-hexyl cyclo-hexanol, di-n-hexyl cyclohexanol, di-tertiary-hexyl cyclohexanol; alkyl and branched alkyl cycloheptanols, e. g., di-n-propyl cycloheptanol, n-secondary and tertiary cycloheptanol, iso-amyl cycloheptanol, corresponding di-amyl cycloheptanols; or polynuclear monohydroxy alcohols, such as alkyl and branched alkyl decalols, e. g., di-methyl decalol, tri-methyl decalol, tetra-methyl decalol, etc., ethyl-methyl decalol, ethyl decalol, di-, tri-, tetra-ethyl decalols, corresponding propyl, butyl, amyl, etc., decalols; bi-alicyclic alcohols having branched alkyl radicals produced by hydrogenating the condensation product of mesityl oxide or isophorone, polyhydro (i. e. saturated) anthracene-oils and alkyl substituted polyhydro-anthracene-ols, e. g., methyl, ethyl, isopropyl, n-, sec-, tert-butyl polyhydro-anthracene-ols, ethyl-isopropyl anthracene-ols, isobutyl-tert-amyl anthracene-oils, etc.; alicyclic mono-nuclear polyhydroxy alcohols, such as alkyl and branched alkyl cyclopentane diols, e. g., ethyl-amyl-cyclopentane-diols, isoopropyl butyl-cyclopentane-diols, sec-butyl-tert-amyl cyclopentane diols, di-iso-amyl-cyclopentane-diols, corresponding cyclohexane-diols; alicyclic polynuclear polyhydroxy alcohols, such as alkyl and branched alkyl deca and polyhydro anthracene-diols, e. g., ethyl deca-diols, di-tri-tetra-, etc., methyl, ethyl, n- and isopropyl, n-iso, sec- and tert-butyl, etc., deca-diols and corresponding (saturated or hydrogenated) anthracene-diols.

Of the many groups of alcohols which are useful for our purpose, the following are preferred: (1) those having at least one and preferably two alicyclic nuclei of six carbon atoms each; (2) those having at least one branched aliphatic radical attached to the alicyclic nucleus, preferably to a 6-atom nucleus; (3) those being free from aryl radicals; (4) those containing a single hydroxy group.

The reason for the particular effectiveness of the described alcohols in the matter of softening normally hard carbon deposits is not definitely known at this time. However, it is known that in order to be effective, the alcohols must possess certain important properties which are: (1) They must have relatively high boiling temperatures so as to remain in the lubricating oil in effective concentration even after prolonged use of the oil. (2) They must be thermally stable, i. e., they must not readily decompose or polymerize under engine conditions. Therefore, they must not contain olefinic double bonds. In particular, they must be sufficiently stable even at the extremely high temperatures to which the top lands of pistons of internal combustion engines are exposed, so that the carbon deposited thereon remains soft. Extended experiments on the relative hardness of carbon deposits formed under various conditions have indicated that the hardness of the carbon depends primarily on the content of oily constituents retained by it. The presence of even small amounts of one or several of the described alcohols in a lubricating oil strangely enough results (under engine conditions) in the formation of an oily, rather than a dry, carbon deposit, even though the oil in the absence of the alcohol may, under the same conditions and in the same engine, deposit a dry and hard carbon. (3) The alcohols must be oil-soluble. Most of the so-called "higher" saturated fatty alcohols of 12 and more carbon atoms, such as lauryl, cetyl, stearyl, etc., alcohols, are very little soluble in hydrocarbon oils. They are solids at normal room temperatures, some of them being waxy, others crystalline. In contrast, the "lower" of our alicyclic alcohols described, i. e., those having between about 12 to 30 carbon atoms, are oily viscous liquids at normal room temperature, while the higher ones are glassy, non-crystalline solids. They are much more soluble in hydrocarbon oils than the fatty alcohols of the same numbers of carbon atoms, and also are much better "softeners" for the transformation of hard carbon to soft carbon.

Acids suitable to form the esters of the above alcohols are primary, mono- or polycarboxylic acids and include fatty acids, both lower and higher, naphthenic acids, wool fat acids, paraffin acids; aromatic carboxylic acids as benzoic, naphthoic, alkyl benzoic or naphthoic, phenyl acetic, phenyl stearic; hydrogenated rosin, carbonic, oxalic, succinic, alkyl succinic, sebacic, agaric, etc., acids. If desired, these acids may contain polar neutral or basic substituents. Suitable substituents are, for example, OH, NH_2, halogen, sulfur, etc., radicals, and examples of the substituted acids are lactic, hydroxy stearic, ricinoleic, amino stearic, hydroxy or amino benzoic or naphthoic, hydroxy or amino phenyl stearic, carbamic, allophanic, thiocarbonic, thiocarbamic or -allophanic, chlorinated or sulfurized fatty acids, etc.

Useful esters may also be derived from certain inorganic acids, such as phosphorous acid, phosphoric acid, arsenous acid, sulfuric acid, etc. Sulfonic acid esters may also be used.

Of the above-mentioned alcohols, a preferred class having from 16 to 30 carbon atoms may be produced by condensing lower aliphatic ketones, such as acetone, methyl ethyl ketone, etc., to products of the type of isophorone or mesityl oxide, further condensing the latter to form bicyclic unsaturated ketones and then hydrogenating the latter to the corresponding alcohol. Also very desirable are the closely related alkylated decalols which may be prepared by hydrogenation of alkyl naphthols.

Preferred esters are amino carbonates, e. g., the carbamates, allophanates, imido carbonates, hydrazine carbonates, etc., of the preferred alcohols, because in addition to carbon modifying properties, these particular esters possess pronounced anti-wear properties. Other desirable esters are the fatty acid esters.

Amounts of the compounds to be added to lubricating oils effectively to modify and reduce the hardness of carbon deposits formed on pistons need not be large. In general, the amounts required vary from about .1%–10%, and preferably from .5% to 5%, depending on conditions to be met.

Methods of manufacture of the cyclic alcohols comprise the above-mentioned condensation of lower aliphatic ketones to cyclic ketones and hydrogenation to the corresponding alcohols; hydrogenation of alkyl naphthols, anthraquinone, etc., to the alcohols; chlorination and subsequent hydrolysis of chlorination products of cyclo paraffins having at least 12 carbon atoms; Grignard reaction applied to open long chain ketones, etc.

The desirable properties of my lubricating oils, containing saturated alicarbocyclic alcohols or esters may be further improved, if desired, by use in combination with certain anti-oxidants, detergents, corrosion inhibitors, extreme pressure compounds, soap thickeners to produce grease, etc. If desired, mixtures of different alcohols of this invention and/or their esters may be used to advantage.

Example I

An S. A. E. lubricating oil, having a viscosity index of 55, containing 2.25% calcium petroleum sulfonate (produced by converting a commercial mahogany soap to the calcium salt), 0.25% phenyl alpha-naphthylamine and 1.0% C_{18} cycloalkyl alcohol was subjected to a 126-hour test in a Caterpillar test engine operated at 850 R. P. M. and at 16.7 B. H. P. At the end of the run the piston rings were free, the piston was clean, and the top land of the piston was free of hard carbon. The metal was not scuffed. What small amount of carbon had deposited at the bottom of the top ring groove was soft and easily removed.

Example II

A lubricating oil of S. A. E. 30 containing 1% of a C_{18} cyclic alcohol was subjected to a 20-hour test in a single cylinder Lauson engine operating at 1700 R. P. M. under conditions known to produce hard carbon, lacquering, etc., with straight mineral lubricating oils. At the end of the run, the piston as it came from the cylinder had a thin coating of soft, velvety carbon which could be rubbed off with a soft cloth, leaving a clean piston having no stuck rings and substantially no top land scratching.

Example III

A sample of western lubricating oil, S. A. E. 20

grade, was divided into two portions. 1% by weight of a bi-alicyclic C_{18} allophanate prepared by condensation of acetone and hydrogenation of the product was dissolved in one portion. Both the blended and unblended portions were tested in the Four-Ball Machine described in Engineering, vol 136, July 14, 1933. This apparatus comprises a set of four steel balls arranged in pyramid formation. The top ball is rotated by spindles against the three lower balls which are clamped in a stationary ball holder. The balls are immersed in the oil to be tested. Six tests were run at 130° C. at 700 R. P. M. under vertical loads of 7 kilograms for a period of two hours. The scar diameters on the balls were then measured and were found to be

Scar diameter: Unblended oil, .70 mm.; blended oil, .21 mm.

The oil improving agents contemplated by this invention may be single compounds or mixtures of these compounds.

Example IV

A sample of western lubricating oil, S. A. E. 30 grade, containing 1% by weight of C_{18} bi-alicyclic allophanate, prepared by condensation of acetone and hydrogenation of the product, was subjected to four 20-hour periods of test in a C. F. R. Diesel engine operating under severe conditions, at maximum B. M. E. P. for the engine, at a load of 2½ H. P. and at a speed of 900 R. P. M. At the end of each 20-hour period, the piston was removed from the cylinder and examined. The carbon and lacquer deposits on the piston crown, top land, ring grooves and on the skirt were unusually soft and rubbed off easily. The bare oil alone, when so tested, yielded a medium hard deposit of carbon and lacquer that would not rub off easily. There was also obtained 24% less wear with the additive oil than with the bare oil.

We claim as our invention:

1. An improved lubricant comprising a mineral lubricating oil having dissolved therein a small amount of an allophanate of an alicarbocyclic alcohol having at least 12 carbon atoms.

2. An improved lubricant comprising a mineral lubricating oil having dissolved therein a small amount of an allophanate of a di-alicyclic alcohol having at least 12 carbon atoms.

3. The lubricant of claim 1 wherein the cyclic radical has at least one branched alkyl radical attached to the nucleus.

4. The lubricant of claim 1 wherein the cyclic radical is free from aromatics.

5. The lubricant of claim 1 wherein the alicyclic radical contains at least one 6 carbon atom ring.

6. An improved lubricant comprising a mineral lubricating oil having dissolved therein .1% to 10% of an oil-soluble allophanate of an alicarbocyclic alcohol having at least 12 carbon atoms.

7. An improved lubricant comprising a mineral lubricating oil having dissolved therein .5% to 5% of an oil-soluble allophanate of an alicarbocyclic alcohol having at least 12 carbon atoms.

PAUL R. VAN ESS.
ELLIS R. WHITE.