

## UNITED STATES PATENT OFFICE

2,257,328

## LUBRICANT

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No Drawing. Application December 7, 1937, Serial No. 178,557

19 Claims. (Cl. 252—39)

This invention relates principally to modified mineral lubricating oils especially adapted to severe service uses as in Diesel engines and aviation engines and similar heavy duty internal combustion engines.

The primary object of the invention is to provide oils of the indicated type which contain materials imparting oiliness and extreme pressure characteristics, as well as stable characteristics, and adapted to overcome tendencies toward the deposition of gums, resins, soot and varnish-like materials upon and about the valves and rings of the indicated types of internal combustion engines, so as to prevent the sticking of such valves and rings, while at the same time overcoming tendencies toward corrosion of certain types of alloy bearings which are especially sensitive to acidic constituents added to the oils or produced in engine operation.

Many mineral lubricating oils commonly used have a strong tendency to develop the above indicated sooty, gummy, resinous and varnish-like deposits so as to interfere with valve and ring operation. These objectionable deposits, which often result in such sticking of valves and rings as to interfere materially with engine operation, are perhaps more often found in the case of Diesel engines and engines operating under similar severe conditions.

I have found that the tendency of mineral lubricating oils to deposit gums, resins, soot and varnish-like materials can be largely overcome by the addition of comparatively small proportions of certain types of materials which have detergent properties when dissolved or dispersed in mineral lubricating oils. By detergency I mean not only that property which aids in lifting or removing, purging or washing away foreign materials which accumulate on the surfaces of valves, rings, pistons or other engine parts, but also that property which prevents the accumulation or deposition of such materials, as distinguished from solvent action upon those accumulations or deposits.

Compositions suitable for this purpose, as I have previously disclosed, belong to the class of compounds known as oil-soluble soaps. These oil-soluble soaps exhibit a permanent state of solubility or dispersion in the lubricating oil, as distinguished from soaps which tend to cloud or gel or stratify, at least in the proportions in which they are used for the present purposes, such proportions being ordinarily between about 1% and 2%, or at least between limits of 0.6% and about 2.5%. Such oil-soluble soaps should have extremely high detergent power, must be stable, and must not polymerize under conditions of use and storage.

Such soaps are found in the oil-soluble metal soaps of normally solid fatty acids which have

been chlorinated sufficiently to render normally solid fatty acids fluid at ordinary temperatures, thereby rendering most of their soaps readily oil-soluble or dispersible as above indicated.

For example, chlorinated saturated fatty acid soaps especially those corresponding to dichloro acid soaps are preferable, specific examples being calcium chlorostearates containing from about 12% to 30% of chlorine based on the acids and especially calcium dichlorostearate or mixtures having a chlorine content corresponding in general to calcium dichlorostearate. For some uses some soaps such as magnesium dichlorostearate are not sufficiently oil-soluble or compatible with lubricating oil to be useful in all instances, and the limitation to freely oil-soluble or dispersible or compatible soap thereby eliminates such objectionable materials.

Again corresponding soaps of unsaturated or normally liquid fatty acids may be employed where the chlorination imparts sufficient stability by reason of the resultant saturation with chlorine, and corresponding soaps such as calcium dichloro oleate may therefore be used. A further type of organic acid soap appropriate for these purposes is that represented by the metal soaps produced from synthetic petroleum acids obtained by known methods from the oxidation of paraffin, "isoparaffins," petrolatum and other heavy petroleum fractions. For example, calcium soaps of such synthetic petroleum acids produced by oxidation are valuable, as are chlorine-containing soaps of such synthetic acids.

Soaps of the above indicated types, have been used by the present inventor to overcome the above indicated valve and ring sticking. In order to employ such soaps in severe service types of internal combustion engines which use alloy bearings particularly susceptible to acidic conditions, and at the same time sufficiently protect such bearings of which cadmium-silver bearings and copper-lead bearings are outstanding examples, I have found that I may incorporate in the oil along with the above indicated types of soaps a relatively high sulfur content, for example 2% to 6% of sulfur. The sulfur content operates to overcome any objectionable action of constituents in the soap upon the bearings. At the same time the soap overcomes any objectionable characteristics exerted by the presence of the sulfur, while permitting the sulfur to exert the full extreme pressure characteristics and oiliness and anti-scuffing or anti-scratching characteristics which it possesses.

## STATEMENT OF INVENTION

In incorporating sulfur according to a preferred form of this invention, I find that it is best accomplished by employing oils having a natural high sulfur content, and I prefer to use oils

which, when refined, still have at least about 2.5% or preferably even higher sulfur content for example 3% to 3.5%. Such naturally occurring high sulfur oils are represented by the Santa Maria Valley (California) crudes, Smackover (Arkansas) crudes, Spindletop (Texas) crudes and some Mexican crudes.

Stated in other words, according to the present invention, the desirable characteristic of overcoming deposition of soot, gums, resins and varnish-like materials by the use of special oil-soluble soaps of the described type (which are different from the ordinary types of soaps sometimes used in the oils for other purposes) is retained in internal combustion engine lubricating oils without fear of attack upon highly corrosion-sensitive alloy bearings, by the expedient of employing a mineral lubricating oil having a high natural sulfur content. By the use of these combined materials the valuable benefits of the sulfur in preventing scuffing and scratching of rings and cylinder walls and imparting extreme pressure characteristics are obtained while overcoming any objectionable features due to the soaps, such as corrosive tendencies. At the same time the beneficial features of such soaps as above indicated are retained, and also the soaps perform a further function of overcoming the objectionable features heretofore recognized in high sulfur-content oils of possessing poor lubricating and wear properties. Thus, each of the addition agents fortunately counteracts the weaknesses of the other agent so that the benefits of both are obtained without any of the disadvantages of either. That is to say, the sulfur protects sensitive alloy bearings such as cadmium-silver and copper-lead bearings against the corrosive action due to the acid constituents of the soaps, and the soap protects against high wear rates and high torque characteristics inclined to be imparted by the sulfur, while the extreme pressure and anti-scratching or anti-scuffing advantages of the sulfur are retained along with the gum and varnish eliminating characteristics of the soaps.

The invention may also be stated as residing in a mineral lubricating oil containing soaps, such as chlorinated fatty acid soaps or chlorinated or unchlorinated synthetic petroleum oxidation acid soaps in quantities to overcome ring and valve sticking in severe service internal combustion engines, in combination with high sulfur content for imparting extreme pressure characteristics and anti-scruffing and anti-scratching characteristics while at the same time overcoming tendencies toward corrosion of sensitive alloy bearings by the acid constituents of the soaps. The invention further applies particularly to such soap-containing oils wherein the sulfur content is obtained by the employment of oils having sufficiently high natural sulfur content, such oils necessarily being naphthenic base oils of so-called Western and Mid-Continent types.

The invention further resides in the employment of soaps of the indicated type in amounts preferably between about 1% and 2%, or between wider limits of 0.6% to 2½%, to overcome ring and valve sticking in high output internal combustion engines such as Diesel and aviation engines without imparting substantial viscosity increase together with oils having a sufficiently high sulfur content to overcome corrosive tendencies of the acid constituents used in conjunction with the soaps to attack the sensitive-type alloy bearings, especially where such sulfur content is

above about 2%, and more particularly where the sulfur content in the lubricating oil employed is from about 2.75% to 4% or 4½% or higher, e. g. 5%, of naturally contained sulfur. At least for some purposes, shale oils, which run as high as about 6% naturally contained sulfur, may also be used after dewaxing if appreciable quantities of paraffin are present. Invention also resides in the incorporation into such oils of additional quantities of excess free fatty acids above those required for the soap but within the limits of the capacity of the sulfur present to overcome the corrosive action of all acid constituents upon corrosion-sensitive alloy bearings.

#### PRACTICING THE INVENTION

In selecting oils containing the required sulfur in natural form, I prefer to employ those crude stocks which contain a sufficient amount of sulfur so that, when distilled and refined as with sulfuric acid for the removal of sludging and other objectionable constituents, sufficient sulfur will remain in the treated distillate to impart the desired characteristics. For example, I have prepared lubricants according to this invention of S. A. E. 30 grade containing between about 3% and 3.5% of naturally occurring sulfur, this lubricating distillate having been treated with 60 pounds of sulfuric acid according to standard acid treating processes. This particular oil was obtained from a Santa Maria Valley (California) crude, and the original sulfur content of the non-acid treated distillate was 4.2%.

The sulfur content ordinarily should be 3% to 4% or more in order that the oil will withstand as heavy a treatment as 80 pounds of sulfuric acid per barrel without reducing the sulfur content to an objectionably low figure. As was indicated above, among other crudes than Santa Maria Valley crudes there are Texas, Arkansas and Mexican oils which may be used. Principal instances are Spindletop and Humble in East Texas and Panhandle, Howard, Ector, Westbrook and Crane in West Texas, in addition to the Smackover crudes of Arkansas and Mexican crudes such as Panuco. All of these oils have natural sulfur contents in excess of 2.5%. Other California crudes which may be employed are Orcutt, Brea and Cat Canyon. In general wax free stocks are preferred, especially as a matter of convenience, but freedom from wax is not essential. Except as to the Orcutt crude mentioned, the other crudes are substantially or sufficiently free from wax.

By judicious selection of stocks to obtain lubricating distillates of sufficiently high sulfur content so that they may be adequately treated with sulfuric acid (up to as high as 80 pounds per barrel if necessary) for the removal of sludge forming material while at the same time retaining preferably at least 3% natural sulfur, a proper lubricating distillate is obtained for blending with the soap required to overcome ring and valve sticking in severe service internal combustion engines.

As illustrative of Santa Maria Valley distillates suitable for the present purposes, the following Table I of specifications is given covering a non-acid-treated distillate and the same distillate treated with various quantities of sulfuric acid in the preparation of an S. A. E. 30 grade lubricating oil. It is obvious that as the S. A. E. grade becomes lighter, for example S. A. E. 20, the sulfur content becomes less.

TABLE I

## Santa Maria S. A. E. 30 lubricating distillate

| Oil                                    | Treated with 98% H <sub>2</sub> SO <sub>4</sub> , pounds per barrel |           |           |           |           |
|----------------------------------------|---------------------------------------------------------------------|-----------|-----------|-----------|-----------|
|                                        | None No. 1                                                          | 15# No. 2 | 40# No. 3 | 60# No. 4 | 80# No. 5 |
| Gravity at 60° F.                      | 16.0                                                                | 16.9      | 18.0      | 18.5      | 19.0      |
| Color N. P. A.                         | Dark                                                                | Dark      | 4.0       | 3.7       | 3.3       |
| Flash C. O. C. °F.                     | 395                                                                 | 400       | 395       | 395       | 400       |
| Fire Point C. O. C. °F.                | 455                                                                 | 455       | 455       | 450       | 455       |
| Viscosity at 100° F.                   | 890                                                                 | 610       | 505       | 475       | 471       |
| Viscosity at 210° F. Say.              |                                                                     |           |           |           |           |
| Univ.                                  | 62                                                                  | 56        | 54        | 53        | 53        |
| Viscosity index                        | -8                                                                  | 10        | 23        | 22        | 24        |
| Viscosity gravity constant             | .912                                                                | .907      | .898      | .895      | .891      |
| Sulfur percent by weight               | 4.2                                                                 | 3.8       | 3.4       | 3.25      | 3.1       |
| Indiana oxidation test:                |                                                                     |           |           |           |           |
| Hours for 10 m. g. per 10 gm. sample.  |                                                                     | 4         | 8         | 14        | 21        |
| Hours for 100 m. g. per 10 gm. sample. |                                                                     | 13        | 27        | 34        | 45        |

All of the above distillates, treated and untreated, are effective to impart film strength or extreme pressure characteristics and to overcome bearing corrosion, but the first three were objectionable on account of sludging tendencies. Therefore, in order to overcome sludging tendencies adequately it is desirable to treat this particular oil with at least 60 pounds of acid per barrel.

The fourth oil listed above, namely that treated with 60 pounds of acid per barrel, was tested in comparison with two other oils, according to the following Table II, employing the Faville-LeVally lubricating-oil testing machine recently placed upon the market and described in papers presented to the Society of Automotive Engineers. This machine gives a measure of both torque and load. It comprises a rotating spindle disposed on a vertical axis, against the sides of which loaded V-shaped jaws are engaged under the influence of means adapted for gradually increasing loads. The results are given in pounds per inch torque at the respective indicated loads, a lower torque figure for any given jaw load being representative of increased oiliness, film strength and extreme pressure characteristics, whereby the relative figures are indicative of the relative values of different oils. The machine is manufactured and sold by the Faville-LeVally Company, 140 South Dearborn, Chicago, Illinois.

TABLE II

## Torque in pounds per inch

| Jaw load | Oil A            | Oil B            | Oil B plus 1.5% calcium soap | Acid treated oil No. 4 of Table I plus 1.5% calcium soap |
|----------|------------------|------------------|------------------------------|----------------------------------------------------------|
| 250#     | 5.75             | 6.25             | 5.0                          | 4.5                                                      |
| 500#     | 10.75            | 11.75            | 9.5                          | 9.25                                                     |
| 750#     |                  | 16.50            | 15.0                         | 14.00                                                    |
| 1000#    | (Seized at 750#) | (Seized at 900#) | (Seized at 1000#)            | 18.00 (Seized at 1100#)                                  |

(Note the higher torque of oil B as compared to oil A, but greater load-carrying ability without seizure. Note that addition of soap to oil B corrects lack of oiliness or slipperiness inherent in high-sulfur oils, without sacrifice of load-carrying ability.)

In explanation of Table II, oil A was a well refined naphthenic base mineral oil from a low

sulfur California crude (Poso Creek), and oil B was a Smackover vacuum distillate untreated except for clay treatment and had a poor oxidation stability. The calcium soap employed in oil B and with oil No. 4 from Table I was the calcium soap of synthetic petroleum acids produced by the oxidation of paraffin wax, which acids are purchasable on the market from the Alox Corporation of Niagara Falls, New York, as "Alox 100 acids"; also "Alox 300 acids" have been used. The whole operation of loading from an initial starting load of 250 pounds up to the point of seizure occupies roughly 30 seconds. The points of contact between the rotating spindle and jaws are lines, there being a line of contact between each side of each of the two V-shaped jaws. As a result of this type of test, the torque under different loads is measurable in pounds per inch for the respective oils, which figures are a measure of the lubricating characteristics of each oil. It is to be noted that in subjecting the three indicated oils to a wear test on the above described machine under a 250 pound jaw load for two minutes, the uncompounded oil A gave a jagged unpolished wear scar on the jaw blocks, whereas oil B gave a large but better polished scar. However, with the addition of the calcium soap to oil B, the wear scar was reduced in size and the polish improved slightly. With oil 4 containing the soap addition, the wear scar was the smallest in size and best in appearance. Thus, in addition to the torque measurement, the examination of the physical characteristics of the wear scars also indicated the relative oiliness or film strength characteristics of the respective oils.

In addition to employing the lubricating distillate containing sufficient naturally occurring sulfur to impart the desired characteristics here described, it is possible, although not a preferred form of my invention, to use a low sulfur distillate or one containing an insufficient amount of sulfur, and to add sulfur thereto in some other form. For example, I may add a sulfurized oil such as a fatty acid type of oil, and more particularly a sulfurized jojoba oil, the latter being a vegetable oil produced from a shrub grown in southwestern United States and in some tropical districts. The peculiar property of jojoba oil resides in its ability to take up as much as 20% to 25% sulfur without turning black and without causing the oils to which it is added to turn black. In using sulfurized fatty acid oil and the like, including sulfurized jojoba oil, a sufficient quantity of such sulfurized material is added to impart in the final lubricant a sulfur content adequate to overcome the tendencies of the soaps to corrode sensitive-type alloy bearings which are to be protected. For example, a few percent of sulfurized jojoba oil containing say 12% sulfur may be introduced in order to add an additional sulfur content of, for example, 0.3% of sulfur to an already existing natural sulfur content of perhaps 0.5% to 0.7%. Other sulfurized oils such as lard oil or sperm oil may be used. Also other types of compounds may sometimes be employed such as di-benzyl di-sulphide or other aromatic type poly-sulphides particularly where halogenated soaps are used. In employing sulfur-bearing addition agents such as those mentioned in this paragraph, the amounts to be employed in general are those to produce an added sulfur content between about 0.25% and 0.75% based on the final lubricating oils. Obviously the free sulfur content must be kept below

those limits which render the sulfur objectionable from any important standpoint.

### SOAPS

As has been indicated, various metal soaps of organic acids may be employed which are oil-soluble, that is which are completely dispersed in or are compatible with the lubricating oil. These include the mentioned calcium chlorostearates and other oil-soluble metal soaps of chlorinated fatty acids, particularly saturated and unsaturated fatty acids having more than 10 carbon atoms and preferably more than 14 carbon atoms, where the chlorine content is sufficient to render the soaps readily oil-soluble (dispersible without cloud) and also, in the case of unsaturated acids, stable by reason of the resultant saturation due to chlorination. In general the desired chlorine content is in excess of 10% and may extend to 40%, being preferably between about 15% and 25% or corresponding to the theoretical 20% in the case of dichlorostearic acid. Other soaps of these acids are aluminum, lead, iron and zinc soaps where adequately oil-soluble, and similarly sufficiently oil-soluble sodium, potassium, copper, cobalt, and nickel soaps and in some instances magnesium soaps although some magnesium soaps have been found sometimes insufficiently compatible with lubricating oil to avoid an objectionable cloud depending on either the character of the acids or the character of the lubricating oil, or both.

However, in general, I prefer to use suitable oil-soluble metal soaps of synthetic petroleum acids produced by controlled oxidation of heavier petroleum fractions such as paraffin wax, petrolatum and lubricating fractions. In general the production of these acids by oxidation is well understood as illustrated by the patents to Burwell Nos. 1,690,767, 1,690,768, 1,768,523, 1,863,004, the James Reissue Patent No. 18,522 and the Sullivan Patent No. 1,789,026 and the various literature citations referred to in said patents. Highly refined lubricating fractions may be employed for these purposes, such as produced by the more modern heavy solvent refinement of dewaxed oils with phenol,  $\text{SO}_2\text{-C}_6\text{H}_6$  mixtures, furfural and the like. The "iso-paraffins" may also be used, by which term I mean the high molecular weight, amorphous paraffinic materials between the heavy lubricating fractions and the crystalline types of paraffins.

Having obtained oxidized oils or paraffinic waxes, the desired acids may be separated according to any known or preferred procedure, such as reacting with an alkali compound like calcium oxide or hydroxide to obtain the formation of calcium soaps from the saponifiable materials present. These soaps are soluble in the oil, or in oil which may be added thereto in the case of waxes, with the result that the oil solution may be filtered to obtain a concentrated soap solution, which in turn may be added in desired quantities to lubricating oil distillates in accordance with the present invention. Again the entire oxidation product may be saponified with aqueous alkali solution, the mass separated by decantation to recover the alkali soaps in water solution and the solution treated with calcium chloride to precipitate the calcium soaps from the aqueous solution. Again the acidic materials may be separated from the oxidation product by any preferred or known means, and the desired soaps such as calcium soaps directly produced therefrom through the medium of

calcium oxide or calcium hydroxide, or the separated synthetic acids may be dissolved in lubricating oil and lime added in the form of either calcium oxide or calcium hydroxide to the solution to form the soap in situ. This soap solution is then heated to about 325° F. to accomplish adequate dehydration, and the solution is then filtered or centrifuged, and diluted with oil to obtain any desired concentration of soap. Substantially complete dehydration is generally necessary (for example to less than about 0.25% water), to insure adequate solubility or dispersibility of the soaps in the oils in which they are to be employed. In fact, similar adequate dehydration is required of all types of soaps employed for the present purpose, for the reason that excessive hydration produces a heavy non-flowable concentrate which will not completely disperse in the oil. Sufficient dehydration is indicated by ready flowability of a concentrate containing 20% to 40% soap, and by ready solubility of the soap or concentrate in the final amount of lubricating oil without cloudiness or at least appreciable cloudiness. It is obvious from the foregoing that soap concentrates are readily produced, and that these are preferable as a means of soap preparation, especially inasmuch as these concentrates may be readily shipped and added to the larger final amounts of oil required for the final lubricating product.

In the case of soaps of the synthetic petroleum acids, other metals than calcium, as outlined for chlorinated fatty acid soaps may be employed in the preparation of these synthetic acid soaps, and used for the present purpose as long as their oil-solubility or dispersibility is adequate. In the preparation of the indicated types of soaps of these synthetic petroleum acids, it is sometimes desirable to boil the concentrates of the final lubricants with a small quantity of water for example about 1% of water, in order to precipitate out an insoluble form which may be removed by filtering and which may sometimes otherwise form in use in the presence of water and precipitate or cause cloudiness.

The synthetic materials herein referred to as synthetic petroleum acids from high boiling paraffinic petroleum fractions as indicated are in fact separated as complex mixtures but these mixtures are relatively free from undesired impurities produced during oxidation and from unoxidized hydrocarbons. In the case of paraffin, any unconverted wax may be separated by any known dewaxing operation. The reaction products from a normal oxidizing operation may contain 20% to 30% of oxidation materials, the greater proportion of which are acidic and are not only in the form of the acids produced but may be also in the form of esters, anhydrides and lactones, all of which acidic or soap-producing materials are of course included within the term "synthetic petroleum acids" or the like.

The acids themselves, with or without the other acidic or soap-forming materials indicated, or such other acidic or soap-forming materials, or the entire oxidation products, may be used in the preparation of soaps for the present purposes, as may seem advantageous or desirable for any given operation or product.

### CHLORINATED SYNTHETIC ACID SOAPS

In addition to the use of the types of soaps of synthetic petroleum acids or acidic or soap-forming materials as above indicated, it may be also desirable, especially for some uses, to produce

chlorinated soaps of such synthetic petroleum materials. Ordinarily these are obtained by chlorinating the synthetic petroleum acids or acidic materials above described either after segregation or otherwise in much the same fashion as described for unchlorinated acids. Chlorination may be readily effected by bubbling chlorine through the materials, following with appropriate neutralization. The soaps of such chlorinated petroleum acids are then prepared in the same manner as indicated for unchlorinated soaps.

Particular reference is here made to the calcium chlorinated petroleum acid soaps, which I have found highly desirable, both when used with the sulfurized oils as herein described and when used in the absence of sulfur-bearing materials. While such chlorinated acids are generally preferred, other halogens may be employed where suitable oil-soluble or dispersible soaps are obtained, and similarly other metals than calcium may be employed where the resultant soaps are sufficiently dispersible in oil.

#### OTHER SOAPS

In addition to the use of the indicated types of metals for the preparation of both halogenated and non-halogenated soaps, suitable organic bases also may be employed such as quinoline bases, nitrogen bases and the alkyl amines such as the ethanalamines, particularly triethanolamines. Sometimes naphthenic acids, both halogenated and non-halogenated may be employed in the preparation of the various metal and organic base soaps mentioned. In this connection a particularly valuable soap to be employed in conjunction with the sulfur-bearing oils hereof may be lead naphthenate or lead chloro-naphthenate especially when used with a natural high-sulfur-content oil described. It is to be noted that the naturally occurring naphthenic acids are distinctly different types of acids from the synthetic petroleum acids described, and at the same time it is also to be observed that both the naphthenic acids and the synthetic petroleum acids mentioned are distinctly different types of acids from the fatty acids herein mentioned as making suitable soaps where the fatty acids are halogenated. In all these instances in order to show an acid of sufficiently high molecular weight, they should contain at least 10 carbon atoms and preferably 14 or more carbon atoms.

#### ACID NUMBER

In general the presence of free acidity (as determined by titration with potassium hydroxide to a phenol phthalein end point) apparently aids in obtaining suitable solutions of chlorinated soaps and oil, and likewise of other soaps mentioned. Also such acidity improves oiliness and extreme pressure characteristics by reason of increased film strength. This free acidity usually represents only a very small percentage of the blended oil, the possible range being between about 0.025% and 0.25% which corresponds roughly to acid numbers of about 0.05 to 0.5, that is mgs. KOH per gm. of oil. Variations on either side of this range have been noted in fairly stable blends, but in general the principle seems to hold that any particular percentage of soap which is prone to excessive increase in viscosity or clouding or sedimentation in the blended oil is usually improved in its blendability by the presence of free acid. For ordinary uses, acid numbers in the lower ranges are perhaps preferable to overcome possible corrosive

tendencies, for example an acid number of 0.2 or less, and perhaps even as low as the indicated figure of 0.05. Again for special short time uses such as breaking-in of new engines, higher acid numbers up to perhaps as high as 0.5 to 0.7 are permissible. Free fatty acid present should, of course, not exceed the ability of the sulfur present in the finally blended oil to overcome the corrosive tendency of the combined acids and soaps.

Ordinarily it is convenient and desirable for the free acid to belong to the same class as that used in making the soap, but other acids such as unchlorinated oleic acid may be added if necessary to obtain the desired acid number should the oil for any reason not already contain a sufficiently high acid number following blending. It has been observed that simple heating and holding of a cloudy concentrate or diluted blend at an elevated temperature, for example at about 325° F. for one hour, improves the compatibility of some of the mentioned soaps in the oil upon cooling, and subsequent titrations usually indicate an increase in acid number without the necessity for any subsequent adjustment or exercise of care to insure acid content. Obviously excessively high free acid content is to be avoided, for example within the upper limits above indicated, because of the possibility of encountering corrosion of certain engine materials such as bushings or bearings, which excessive acid number the amount of sulfur present in the oil may not be able to offset. However, so long as the sulfur content present is sufficient to overcome such corrosive tendencies, the acid number apparently does not need to be otherwise restricted.

*Controlling acidity.*—Where it is necessary to control the acidity by further reduction thereof, the same may be accomplished by further treatment with a base such as additional lime, or triethanolamine or kindred amines such as triethylamine or morpholine, or aqueous or alcoholic solutions of sodium or potassium hydroxide, or mixtures of these. For example, when a soap concentrate containing calcium dichlorostearate yielded a blended oil of 0.7 acid number when diluted to a soap content of 1.3%, further heating of the concentrate before blending to around 325° F. with an additional quantity of lime reduced the acid number in the final diluted blend to 0.4, and a further reduction of acid number to only 0.2 was obtained by further treatment of a portion of the concentrate, before blending, with 0.5% triethanolamine added at 250° F. and carried up to 325° F. For the most efficient re-neutralization, small amounts of water, 0.05% to 0.2%, may be used along with the lime, which may vary from 0.05% to 0.2% in a 1% to 2% soap blend. In all of these soap-producing operations substantially complete dehydration is effected in conjunction with the operation; for example, the water is reduced to less than about 0.05% in the final blend. In connection with such further neutralization of concentrates with aqueous or alcoholic solutions of sodium or potassium hydroxide, either with or without additional lime, acid numbers have been reduced to as low as 0.05 on finished engine lubricants containing 1.3% total soaps. For example oils so reneutralized with concentrated KOH have been found non-corrosive to bronze wrist pin and Babbitt crank shaft bearings even without the use of sulfurized materials. In all these operations it is, of course, desirable to filter the final

blended products for the removal of precipitated solids, or unreacted lime or the like. This is of course especially true in the event that decolorizing earths such as refined diatomaceous earth have been used, this applying either to the concentrate or to the finally blended oil as conditions may indicate. For example in a soap-oil concentrate containing around 40% soap with acid numbers of below about 1.5, the tendency is for the concentrate to become cheesy. In this instance the filtering will be left until after the final blending operation wherein final dehydration can be effected by the accompanying heating.

It is obvious that, in addition to soaps and sulfur materials of the type indicated, other agents may be added if necessary such as other known oiliness and film strength agents. For example where metal soap such as calcium soaps of synthetic petroleum acids from the oxidation of high boiling paraffinic petroleum fractions are employed and it is desired to impart some further oiliness characteristic beyond that imparted by the sulfur, a chlorinated material such as methyl dichlorostearate may be introduced or chloro naphthalene, or chlorinated paraffin or chlorinated naphthenates.

Further, soaps such as calcium phenyl stearate or calcium chloro phenyl stearate may be employed, in the sulfur-bearing oils hereof, or aluminum naphthenate, or aluminum naphthene plus aluminum stearate where the naphthene acts as a solubilizer for the stearate. Unsaturated fatty acid soaps of sufficient oil-solubility or compatibility may be used sometimes without chlorination or other modification, such as calcium oleate.

In view of the foregoing, it will be apparent that the use of the oil-soluble soaps is desirable to overcome valve and ring sticking as well as wear but when occurring alone not entirely desirable from the standpoint of corrosion of alloy bearings of the sensitive types represented by cadmium-silver and copper-lead. It is also apparent that the use of the sulfur compounds alone is not so desirable from the standpoint of lubricating and running-in properties and from the standpoint of wear but the sulfur compounds are desirable from the standpoint of overcoming scratching and scuffing of rings and walls and of imparting high pressure characteristics. With the combination of both soaps and sulfur content, especially naturally appearing sulfur, the one material overcomes the bad characteristics or weaknesses of the other, and all combined valuable properties of both are retained. At the same time objectionable effects of the sulfur upon the iron appear to be overcome. The result is a compounded lubricant having non-corrosive characteristics with respect to even the most sensitive alloy bearings, and also having extreme pressure and anti-wear characteristics, and further having characteristics of preventing ring and valve sticking in severe service internal combustion engines by the prevention of or solubilizing or peptizing of gummy, resinous and varnish-like materials which otherwise tend to accumulate on metal surfaces. These oils are freely fluid oils not possessing any appreciable or noticeable increase in viscosity over corresponding lubricating oils of like grade, or in other words free from greasing consistency.

It is to be understood that the foregoing disclosures are to be taken as illustrative of the in-

vention claimed rather than as limiting thereof. I claim:

1. A freely fluid lubricating oil containing between about 0.6% and 2.5% of an oil-soluble metal soap of organic acids containing at least about ten carbon atoms and adapted to overcome valve and ring sticking tendencies, the oil containing non-corrosive sulfur naturally-occurring in the oil in small quantity to overcome corrosive tendencies of the soaps with respect to corrosion-sensitive alloy bearings and to impart oiliness and extreme pressure characteristics, the sulfur being present in amounts insufficient to exert corrosive and unstable characteristics in the presence of the soap.

2. A distilled mineral lubricating oil of naphthenic base having normally fluid and non-greasing characteristics containing between about 0.6% and 2.5% of an oil-soluble metal soap of an organic acid containing at least about ten carbon atoms to the molecule and adapted to overcome tendencies in the oil to deposit gummy and resinous materials resulting in tendencies to cause valve and ring sticking in internal combustion engines, the oil having a non-corrosive sulfur content naturally-occurring in the oil between about 2% and 6% and adapted to overcome corrosion tendencies on corrosion-sensitive alloy bearings affected by said soaps.

3. A mineral lubricating oil for severe service internal combustion engines comprising a naphthenic base lubricating oil containing between about 0.6% and 2.5% of an oil-soluble metal soap of an organic acid having at least about ten carbon atoms, the soap having otherwise mildly corrosive tendencies, the oil having a content of chemically combined substantially non-corrosive sulfur in the form of sulfur naturally occurring in a lubricating oil, in amount less than about 6% adapted to overcome corrosive tendencies of the soaps, the soaps also being adapted to overcome the corrosive tendencies of the sulfur present, the oil being freely fluid at normal temperature, non-corrosive to ferrous surfaces and to corrosion-sensitive alloy bearings, and being free from grease-like characteristics.

4. A mineral lubricating oil for severe service internal combustion engines containing a quantity of oil-soluble metal soap of organic acids adapted to overcome valve and ring sticking tendencies and having a content of chemically combined substantially non-corrosive sulfur naturally occurring in mineral lubricating oil in amounts of about 2% based on the oil to impart extreme pressure and anti-scuffing characteristics and to overcome corrosive tendencies imparted by the soaps toward corrosion-sensitive alloy bearings, the oil being free from corrosive characteristics and from grease-like characteristics and being normally fluid and free from substantial increase of viscosity over the original base oil.

5. A mineral lubricating oil according to claim 1 having an acid number between about 0.2% and 0.5%.

6. A mineral lubricating oil according to claim 1 containing a small quantity of a free organic acid of the general type of that from which the soap is formed.

7. A mineral lubricating oil according to claim 1 wherein the soap is a soap of synthetic petroleum acid produced by the oxidation of heavy petroleum fractions in the class consisting of paraffin, iso-paraffin, petrolatum and lubricating fractions.

8. A mineral lubricating oil according to claim 2 wherein the soap is an oil-soluble metal soap of synthetic petroleum acids produced by oxidation of heavier petroleum fractions.

9. A mineral lubricating oil according to claim 2 wherein the soap is oil-soluble metal soap of acid from a class consisting of fatty acids, halogenated fatty acids, synthetic petroleum acidic materials, produced by oxidation, halogenated synthetic petroleum acidic materials from oxidation, phenylated fatty acids, and naphthenic acids.

10. A lubricating oil possessing high film strength containing as essential ingredients a mineral lubricating oil having a non-corrosive sulfur content naturally occurring in the oil sufficient to impart extreme pressure characteristics and containing a quantity of oil-soluble metal soap of organic acid having at least 10 carbon atoms, the soap being present in quantities sufficient to impart added oiliness to the oil and to overcome corrosive tendencies of the sulfur, and the sulfur being present in quantities sufficient not only to impart said extreme pressure characteristics but to overcome any corrosive tendencies of the soap with respect to metals highly sensitive to acidic corrosion, the oil product being normally fluid and free from substantial increase in viscosity and grease-like characteristics.

11. A mineral lubricating oil according to claim 10 wherein the soap is soap of synthetic petroleum acids produced by oxidation of high boiling paraffinic petroleum fractions.

12. A mineral lubricating oil according to claim 10 wherein the soap is soap of organic acid from the class consisting of halogenated fatty acids, synthetic petroleum soap-forming materials from

the oxidation of petroleum fractions, halogenated synthetic acids from the oxidation of petroleum fractions, phenylated organic acids and naphthenic acids.

13. A lubricating oil according to claim 10 wherein the soap is calcium chloro stearate possessing a chlorine content between about 12% and 30%.

14. A lubricating oil according to claim 10 wherein the soap is a calcium soap of synthetic petroleum soap-forming materials produced by the oxidation of high boiling paraffinic petroleum fractions of the class consisting of highly refined lubricating oils, paraffin, amorphous paraffins and petrolatum.

15. A mineral oil according to claim 10 wherein the soap is a calcium soap of chlorinated synthetic petroleum acidic materials obtained by oxidation of high boiling paraffinic petroleum fractions.

16. Mineral lubricating oil containing an oil-soluble soap of organic acids having the characteristic of overcoming deposit of gummy and resinous materials and also having naturally-contained non-corrosive sulfur to overcome corrosive characteristics of the soap, the product being in liquid form and free from grease-like characteristics.

17. An oil according to claim 1 in which the non-corrosive sulfur content is between about 2% and 6% based on the oil.

18. An oil according to claim 10 in which the naturally-occurring non-corrosive sulfur in the oil is between about 2% and about 6% of the oil.

19. An oil according to claim 16 in which the sulfur naturally-occurring in the oil is between about 2% and about 6%.

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