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LUBRICANT

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This invention relates primarily to modified mineral lubricating oils, the general object of the invention being to supply to lubricating oils, oiliness and stabilizing constituents capable of imparting extreme pressure characteristics and also of overcoming the deposition of soot, gums, resins and varnish-like materials upon and about the valves and rings of internal combustion engines, and of preventing the sticking of rings and valves especially in engines of the Diesel type where operating conditions are in general rather severe, and also in high output aviation engines. This is a continuation in part of my copending application, Serial No. 121,167.

In the case of many lubricating oils there has in the past been a strong tendency toward the development of resinous and similar deposits about valves and rings of internal combustion engines due principally to the lubricating oil used, although in part to the fuel in some instances. 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.

Preliminary

Soaps.—The compositions suitable for this purpose belong to the class of compounds known as oil-soluble soaps. It is preferred to employ an oil-soluble soap having extremely high detergent power. At the same time such oil-soluble soaps must be stable, must not polymerize under conditions of use and storage, and must exhibit a permanent state of solubility or dispersion in the lubricating oil. The soaps of unsaturated fatty acids such as calcium oleate are commonly known to be soluble in mineral oil, but these soaps of unsaturated acids are unstable under engine operating conditions and produce sludge by polymerization or oxidation. The soaps of saturated fatty acids, such as calcium stearate are relatively more stable toward oxidation and heat, but such soaps of saturated fatty acids are in general insufficiently soluble in lubricating oil at atmospheric temperatures for their solutions to show sufficient detergent properties. It is possible to obtain temporary super-saturated solutions or dispersions of calcium stearate in lubricating oil having sufficient soap content to exhibit satisfactory detergent properties under engine operating conditions, but such super-saturated dispersions are apt to gel, cloud or stratify during storage, thereby making such suspensions practically of no value in commercial operations.

Soap-solubility in mineral lubricating oils.—I have found that saturated fatty acids, such as stearic and palmitic acids which are solids at normal temperatures and relatively insoluble in mineral oils at ordinary temperatures, can be converted into a liquid state at normal temperatures which permits practically unlimited solubility of the acids in the oils at ordinary temperature, by the expedient of chlorination of such otherwise high melting point and oil-insoluble fatty acids. For example stearic acid which has a melting point of about 160° F. ceases to be a solid at ordinary temperatures and becomes liquid when as little as two chlorines are introduced into the molecule, thereby producing dichlorostearic acid which corresponds theoretically to 20.1% chlorine. The indicated soaps of such acids also are readily soluble or dispersible in mineral lubricating oils. I may sometimes use other halogens, such as fluorine, bromine or iodine, but in general I prefer to use chlorine. However, it is to be understood that my invention is not limited necessarily to any particular halogen.

Besides the soaps above indicated, other appropriate oil-soluble halogenated fatty acid soaps and halogenated synthetic petroleum acid soaps may be employed. Soaps of normally solid unsaturated fatty acids, such as elaidic acid, when chlorinated are useful, because of both lowered melting point and stabilization by reason of the saturation produced by the entry of chlorine at the double bond. Likewise soaps of normally liquid unsaturated fatty acids, such as oleic acid, when chlorinated become valuable because the consequent saturation with chlorine at the double bond stabilizes them by overcoming susceptibility to oxidation and polymerization. The synthetic petroleum acid soaps are those from such acids as are produced by oxidation of petroleum fractions

to yield oil-soluble synthetic acids of fairly high molecular weight. These synthetic petroleum acids are neither fatty acids nor naphthenic acids, and usually carry ketone, aldehyde, and/or hydroxy groups in addition to the acid carboxyl groups.

Suitable oil-soluble soaps of these various chlorinated acids preferably are soaps of alkaline earth metals and heavy metals in general, for example, calcium, aluminum, lead, iron and zinc. Calcium soaps are especiallly valuable. Other possibilities for soaps of such acids are sodium, potassium, copper, cobalt and nickel soaps when oil-soluble, and possibly in some instances magnesium soaps, that is, where such magnesium soaps are sufficiently oil-soluble or compatible with lubricating oil. It may also be possible to employ soaps of chlorinated naphthenic acids.

Statement of Invention

Broadly stated, the invention resides in a lubricating oil otherwise possessing the properties of forming sooty, gummy, resinous and varnish-like deposits upon and about valves and piston rings of internal combustion engines, especially Diesel engines, where said lubricating oil contains a small quantity, but sufficient however to avoid substantial deposits of such objectionable materials, of an oil-soluble metal soap of acids of the type of halogenated saturated and unsaturated fatty acids and halogenated synthetic petroleum acids of relatively high molecular weight, i. e., having not less than about ten carbon atoms, and preferably fourteen or more carbon atoms, to the molecule. For these purposes the soaps are to be employed in the oil to the extent of about 1% to 2%, for the reason that substantially greater amounts of soaps tend ordinarily to thicken the oils undesirably and to form excessive amounts of ash in the combustion chamber resulting in high rates of wear of the top piston ring and heavy ash deposits on the cylinder head and exhaust valves, whereas considerably smaller quantities, for example about ¼% or less, ordinarily do not impart sufficient stabilizing capacity to avoid or overcome deposition of gums, resins and the like. These oils also possess improved film-strength or load-carrying capacity. The invention resides further in oil containing such soaps as above indicated for the indicated purpose wherein the oil itself is especially adapted to the severe uses encountered in Diesel engines and the like. Such an oil preferably is a naphthenic base oil which in itself affords some solvent characteristics for gums, resins, and varnishes. On the other hand, highly refined or highly paraffinic oils may be employed at least for some uses and/or with certain of the soaps such as the calcium soap of chlorinated synthetic petroleum acids produced by oxidation of paraffin, petrolatum or paraffinic raffinates.

Not only are the mentioned chloro-acids readily oil-soluble but the calcium soaps therefrom are likewise readily oil-soluble. While more than two chlorine atoms may be introduced into each molecule both as to saturated and unsaturated acids, I have found that in general two chlorine atoms are sufficient to reduce the melting point of the acids to permit adequate solubility of both the acids and their appropriate soaps, particularly calcium soaps, in mineral lubricating oil. In the case of the unsaturated acids this chlorination effects the further desirable elimination of the double bond, thereby overcoming objectionable effects of the unsaturation such as susceptibility to oxidation and polymerization. On the basis of these acids, the chlorine content may therefore be considered as ranging between approximately 15% and 25% according to the molecular weight of the acid. For example, dichlorostearic acid has a theoretical chlorine content of 20.1%. Broadly, the chlorine content may be varied from 10% to 40%.

Therefore, the invention further resides in lubricating oils otherwise possessing the properties of forming sooty, gummy, resinous and varnish-like deposits on valves and rings of Diesel engines and the like, such oils containing a small proportion in the order of 1% to 2% of soaps of chlorinated fatty acids, either saturated or unsaturated, with a chlorine content which corresponds approximately to dichloro-acids or somewhat less, and in general is between about 15% and 25% of chlorine based on the acid, or about 20%. The invention particularly applies where such soaps are calcium soaps, but may be extended also to aluminum and other equivalent soaps as indicated herein. More broadly the invention also resides in the use of such chlorinated material containing from 10% to 40% chlorine.

My invention also includes other various novel features, uses, combinations, proportions, compositions and methods herein disclosed, such as the use in the indicated types of lubricating oils of mixtures of calcium chlorostearates with other soaps such as calcium phenyl stearate or with additional oiliness agents, corrosion inhibitors, stabilizing agents and solubilizing agents such as esters of fatty acids or synthetic petroleum acids, amines, alcohols and ethers. The invention may also include sulfurized or phosphorized fatty acid or other organic acid soaps herein disclosed as substitutes for the chlorinated soaps herein disclosed.

I have also discovered that oil-soluble metal or organic base soaps of non-halogenated acids of the types above described may be combined as one component of a double-component addition material with any type of oiliness or film strength agent as a second component. Such a second constituent may be methyl alpha alpha dichlorstearate, other oiliness agents of the same type produced from other alcohols such as ethyl and amyl alcohols and other chloro-acids such as chloro-phenyl stearic, chloro-oleic, chloropalmitic and similar acids; chlorinated naphthalene; chlorinated paraffin; sulfurized or chlorinated lard oil or sperm oil or jojoba oil; chlorinated diphenyl oxide; esters of synthetic petroleum acids; esters of chlorinated synthetic petroleum acids; tricresyl phosphate, and in general all other types of oiliness or film-strength-improving agents or mixtures thereof.

Therefore the invention may also be stated as extending to the use in mineral lubricating oils of an oil-soluble soap constituent combined with an oiliness or film-strength-improving element or constituent, such as one or more sulfur or chlorine atoms or phosphorous groups and the like, contained either in the soap itself, and/or contained in a second additive component.

In this respect, the invention also includes soaps made with organic bases such as triethanolamine, quinoline, nitrogen bases from petroleum, and the like. Such organic base soaps may be used as substitutes for said oil-soluble metal soap when that soap is not chlorinated and is required to be used in a two-component additive material. When such an organic base soap is

chlorinated it may be used as a substitute for the oil-soluble metal chlorinated soaps either as a single component additive or in conjunction with other additive agents. Soaps appropriate for this purpose are represented by triethanolamine naphthenate, triethanolamine chloro-naphthenate, triethanolamine chlorinated fatty acid soaps and other similar soaps of acids herein mentioned. Usually, however, the organic base soaps are not used except in small proportion in conjunction with metal soaps, for example, 1% of calcium dichlorostearate with 0.3% of triethanolamine dichlorostearate.

The invention also includes reneutralization, as in an oil-soap concentrate or blended oil where the acid number is too high, to reduce to a maximum acid number, such as 0.2, by the use of more of the original base or the addition of another base, and in the latter connection, the above mentioned organic bases such as triethanolamine are valuable and result in a mixture of soaps.

The invention also resides in oil-soap concentrates herein described, as well as in the finally blended oils, especially as such concentrates are substantially completely dehydrated and are therefore fluid at normal temperatures and readily miscible with lubricating oil, especially of the naphthenic type.

While I do not wish to be limited by theory, the following explanation will aid in understanding my invention. A stable oil-soluble soap of high detergent power is effective in preventing ring sticking, and also increases the "oiliness" of the compounded oil to give improved lubrication under light or mild service conditions over straight mineral oil, due to preferential adsorption of the carboxyl group of the organic acid radical of the soap on the metal surfaces. As the temperature and pressure increase under heavier loading and higher power output, the adsorbed layer of soap or acid constituent thereof breaks down, permitting metal to metal contact resulting in a scuffing, galling, scratching, and eventual failure of the engine. Under these severe conditions, the high film strength element essential to my invention comes into play and prevents disruption of the lubricating film. The high temperature apparently activates the film strength element, chlorine for example, causing it to displace the more mild oiliness agent of the soap or organic acid type in the adsorbed layer. The rate of apparent wear is probably greater when chlorine or liberated HCl is responsible for the adsorbed layer, and, while a higher rate of wear is preferable to complete failure in emergencies, it is therefore better not to have the active chlorine type of adsorbed layer in effect at all other times. In the compositions shown herein, there is provided in addition to the active film strength agent such as chlorine, an oxygenated type of oiliness agent in the form of the carboxyl group of a soap, ester, or free fatty acid or ketone, aldehyde, ether or alcohol radical; said oxygenated agents being intended to provide the adsorbed lubricating layer and displace the high film strength agent therefrom under ordinary operating conditions. Thus an outstanding feature of my invention consists in providing in a compounded lubricating oil an oiliness agent of the oxygenated type for use under normal operating conditions and a higher film strength agent which becomes active and rescues the lubricating film under emergency conditions. Insofar as specific soaps herein disclosed are new in lubricants, the invention also extends to the use of such soaps in lubricating oils in sufficient quantities and with necessary hydration to produce greases having severe service characteristics similar to those of the lubricating oils described.

Description in Detail

In practicing the present invention, any otherwise satisfactory mineral lubricating oil is selected. As above indicated, this is preferably a naphthenic base or Western type oil, especially where such an oil is to be used for Diesel engine lubricating oil. On the other hand with chlorinated synthetic petroleum acid soaps, for example, I have employed successfully paraffinic oils.

According to one form of the invention, I add to such an oil approximately 1% to 1.5% of a soap capable of preventing the formation and/or accumulation of gums, resins and varnishes upon and about rings and valves of internal combustion engines. While the amount of such soaps may be varied between about 0.5% or 0.6% and about 2%, I prefer to use approximately 1.3% or between about 0.8% or 1.0% and 1.75%, inasmuch as such proportions have so far proved most beneficial.

The soaps which I have found to be highly satisfactory for these purposes are especially the alkali earth metal soaps of halogenated fatty acids and of halogenated high molecular weight synthetic petroleum acids. In general such halogenated materials are the chlorinated materials. For example the calcium soap of chlorinated stearic acid has been found highly efficient. Similarly, the calcium soap of chlorinated oleic acid is very desirable. Both the calcium dichlorostearate and the calcium dichloro-oleate function adequately in the proportions above indicated to yield a highly satisfactory oil for Diesel engine or similar uses, the performance of the two oils being much the same, although the two chlorine atoms are presumed to be attached to the 9th and 10th carbon by direct addition in the case of the chlorinated oleic acid, whereas in the case of the saturated stearic acid the two chlorine atoms are attached by substitution to the alpha and/or some other carbon probably close to the carboxyl group. Similar positions may be assumed in the case of the synthetic petroleum acids.

In the case of chlorinated stearic acid, I have found that whereas calcium stearate cannot be used alone on account of lack of oil compatibility, a substantial amount of calcium stearate can be employed when a larger quantity of calcium dichlorostearate is present. In other words, the soluble calcium chlorostearate soaps have a solubilizing action on unchlorinated calcium stearates.

Chlorine content.—While the chlorine content of the halogenated acids used may range from 10% to 40%, for the sake of simplicity I may refer generally to a chlorine content of about 15% to 20%, corresponding roughly to two chlorine atoms introduced into the acid molecule, as being typical of my invention; for example, dichloro-stearic acid and dichloro-oleic acid. Apparently mixtures are obtained containing from 1 to 3 or 4 or even more chlorine atoms per molecule, and in using these materials it is satisfactory to use products containing from about 17% to 21% or even within a range sometimes of 15% to 25% or 30%, the above men-

tioned wider range of 10% to 40% chlorine being also within the scope of the invention.

The introduction of only one chlorine atom causes apparently a marked lowering in the melting point of the normally solid acids such as stearic acid, but the introduction of two chlorines per molecule yields an acid thoroughly liquid at temperatures as low as —20° F. in the case of stearic acid. The mono-chlor derivative of stearic acid corresponds to a chlorine content of 11.2% while the dichlor derivative corresponds to a chlorine content of 20.1%. The chlorination may be continued to incorporate more than two chlorine atoms in each molecule of the acid if desired, the trichlor-derivative of stearic acid having 27.4% chlorine, but I have found that two chlorine atoms generally are sufficient to reduce the melting point to the desired degree and to improve the solubility of the acid and its soaps in mineral lubricating oil to the point where it may be used in practicing my invention. Usually a mixture is obtained on chlorination containing unchlorinated acid as well as acids carrying one, two or more chlorine atoms per molecule. Thus, chlorinating any particular acid to achieve a predetermined chlorine content corresponding to a theoretical dichloro-acid (i. e. 20.1% chlorine in the case of stearic acid) does not give a material which is pure dichloro-acid. To study the behavior of the pure acids, the chloro-products must be resolved into the various species. However, in practical operations it has been found possible to use the overall chlorine content as a guide in obtaining suitable materials for practicing my invention.

Unsaturated fatty acids which also are solid at normal temperatures, such as elaidic acid, can be converted into lower melting point acids by the simple addition of chlorine at the double bond of the hydrocarbon chain. Liquid unsaturated fatty acids, such as oleic acids, are improved by chlorination, not so much as regards melting point and solubility in mineral oil, but as regards susceptibility to oxidize and polymerize at engine temperatures by reason of the elimination of the double bonds at which the chlorine enters as in the case of the two chlorine atoms in dichloro-oleic acid.

Chlorinated soaps.—When I have reduced the melting point of the normally solid fatty acids by chlorination sufficiently to achieve miscibility of the fatty acids with lubricating oil at ordinary temperatures, I find that the calcium soaps of such chlorinated fatty acids are also soluble in the lubricating oil to a greater extent than the calcium soaps of the corresponding non-chlorinated fatty acids. Thus, by chlorinating fatty acids I am able to produce synthetic acids which yield soaps of greatly improved solubility in mineral lubricating oils. Also, when I use unsaturated fatty acids as raw materials, I produce synthetic acids having no unsaturated double bonds and thereby correct the abnormal oxidizing and polymerizing tendency of the original fatty acids. Thus by chlorination I can now use the calcium soaps without danger of the abnormal oxidation or polymerization resulting from the unsaturated linkages of the original unsaturated fatty acids. While I do not wish to be limited by theory, it appears from experimental research that the exact location of the chlorine atoms in the hydrocarbon chain is not critical. The main requirement is that sufficient chlorine be incorporated to insure compatibility of the chlorinated acids and especially the soaps produced therefrom with the mineral lubricating oil to be employed. As a further feature of my invention, the chlorinated soaps are not only soluble themselves in oil, but have the property of increasing the oil solubility or compatibility of otherwise relatively insoluble or incompatible unchlorinated soaps. This makes it unnecessary to remove all of the unchlorinated acids from the reaction products obtained upon chlorinating, say, stearic acid.

I have found that, as a general practice, soaps which are most readily compatible with mineral oils are produced from acids which are miscible with lubricating oil in all proportions. However it is not true that all acids which are miscile with lubricating oils will necessarily yield soaps which are compatible with or soluble in such lubricating oils. A notable example of such an insoluble soap is found in the case of the soaps of the low melting point saturated acids from cocoanut oil. These acids owe their low melting point and ready miscibility with such mineral lubricating oils to their low molecular weights, but the calcium soaps of these low molecular weight acids are relatively insoluble in ordinary lubricating oil. The chlorination of these low molecular weight fatty acids improves the solubility of these calcium soaps in lubricating oils, but for the best results I prefer higher molecular weight acids such as stearic, palmitic, arachidic, oleic, margaric and elaidic acids.

In general such fatty acids are those which contain preferably fourteen or more carbon atoms, and yield soaps readily "soluble" or compatible with mineral lubricating oils, of which naphthenic base oils are desirable examples. For the purpose of obtaining the increased film strength which I have discovered necessary, I may chlorinate such liquid acids as phenyl stearic acid which already yield oil-soluble calcium soaps.

Position and number of chlorine atoms.—As has been indicated above, experimental research makes it appear that the exact location of the chlorine atoms is not critical. For example, chlorination of the unsaturated oleic acid with two chlorines will result in the simple addition of the two chlorine atoms at the double bond, that is theoretically on the 9th and 10th carbon atoms in the chain. On the other hand, chlorination to introduce two chlorine atoms into saturated acids such as stearic or palmitic acid will theoretically cause the chlorines to enter close to the COOH group. It is probable that in most instances the two chlorines will enter on the alpha carbon by substitution for the hydrogens, but it is possible that they might enter on the beta carbon or on the gamma or on any other carbon, or on two different carbons, or on different carbons in different molecules. For the sake of this description, it may be convenient to assume that both chlorine atoms enter on the alpha carbon without, however, restricting me to any such theory.

Film strength.—I find that chlorination of fatty acids not only yields calcium soaps sufficiently soluble in mineral oil to give the required detergent action to prevent ring sticking, but the presence of chlorine also imparts improved oiliness and film strength to finished compounded lubricating oils. As an example, an acid treated naphthene base oil of 21.0° A. P. I. gravity at 60° F. and 54 seconds Saybolt Universal viscosity at 210° F. was found to carry a maximum load of only 5 pounds on a Timken film strength test-

ing machine, but when compounded with 1.3% of calcium dichlorostearate the same oil carried a load of 35 pounds on the Timken machine. The film strength on the Almen machine was raised from 6 pounds to 12 pounds, and on the S. A. E. machine from 60 pounds to 440 pounds at 250 R. P. M., rubbing ratio 14.6 to 1, and a loading rate of 75 pounds per second. (For descriptions of these machines, see S. A. E Journal, vol. 28, 1931, pages 53 to 60, and vol. 39, 1936, pages 293 to 296.)

In actual Diesel engine operation, it was determined that in a particular engine, the non-compounded oil could be used only up to 90 pounds per square inch brake-mean-effective pressure loading of the engine without scuffing rings and cylinder wall, whereas after compounding with the 1.3% calcium dichlorostearate, the oil was able to carry a loading of 106 pounds brake-mean-effective pressure which is the maximum power that could be developed by the engine without supercharging. Under the severe conditions of overloading in comparison with the normal operating brake-mean-effective pressure of 75 pounds per square inch, perfect lubrication was obtained with the compounded oil.

In break-in tests on engines fitted with new liners, pistons and rings, it has been found that, with the compounded oil containing calcium chlorostearate, full normal operating load can be safely applied after only one hour of running-in, as compared with a customary 15 to 18 hour running-in period. Furthermore, after 100 hours of normal full load operation the surfaces of the liners and ring faces are in materially better wearing condition when the compounded oil is used after only a one hour break-in period, than when the uncompounded oil is used after a seventeen hour break-in period with the uncompounded oil. The better running-in and wearing properties of the compounded lubricant are shown in the wear figures obtained in carefully controlled tests run continuously at normal full load; the cylinder wear being 0.0004 inch per 1000 hours for the non-compounded oil and only 0.0008 inch per 1000 hours for the compounded oil.

The compounded oil containing an oiliness component of the oxygenated type and a high film strength agent for emergency conditions should show a minimum film strength of 15 lbs. on the Timken machine or 9 lbs. on the Almen machine.

Production of Chloro Acids

Chlorostearic acids.—As a convenient means for practicing the invention, soaps of the chlorostearic acids, particularly the calcium soaps, will be considered without however indicating any exclusion of the other chloro-organic acids and their soaps herein mentioned. While I have referred above to a simple chlorination of the various acids by bubbling free chlorine through the acids in liquid or melted condition, it will be apparent that other means may be employed, such as treating the alkali soap solution of unsaturated acid (e. g. sodium oleate) with hypochlorite, or dissolving oleic acid in a solution of sodium hypochlorite.

Direct chlorination.—Direct chlorination of the saturated acids may be effected in liquid or melted form directly by bubbling chlorine therethrough at temperatures of 175° F. to 240° F. in the absence of any diluent or the like. Preferably the temperature is controlled to not over 220° F. during chlorination. Again chlorination may be effected by bubbling chlorine through a solution of the saturated acids, for instance where the acids are dissolved in a diluent such as carbon tetrachloride or methyl alcohol, such fluid diluent being condensed and refluxed during the operation.

Purification.—Having obtained the acids with a suitable chlorine content as hereinabove indicated and having eliminated the volatile diluent where such may have been used, purification may be effected by fractional crystallization where it is desired to remove unchlorinated or insufficiently chlorinated acids. Or when the material is chlorinated in the presence of a diluent such as carbon tetrachloride, the desired chlorinated acids may be separated by cooling to the desired degree, e. g., 0° F. and simply cold pressing; or chlorinated materials can be diluted, cooled and cold pressed, whereby the materials crystallized at the respective temperature are recovered on the filter. The unchlorinated or only partially chlorinated (mono chloro) acids separated on the filter may be recycled to the chlorination process if desired.

Where a diluent is used in chlorinating, after sufficient chlorination the flow of the chlorine is stopped and the mixture is blown with a neutral gas such as flue gas or CO_2 or natural gas or nitrogen or subjected to vacuum for the purpose of removing the free chlorine and dissolved hydrochloric acid; the mixture is then cooled, and filtered or settled or centrifuged; and then the materials are heated for the recovery of the solvent or diluent. Necessarily, high temperatures must be avoided to prevent liberation of hydrochloric acid. Fractional crystallization is preferred as distinguished from fractionation by distillation on account of decomposition and splitting out of HCl when attempting fractional distillation.

Preparation from chlorinated esters.—As another means of obtaining the chlorostearic acids, stearic acid may be reacted with methyl alcohol to produce methyl stearate and this material treated with chlorine to yield methyl-chlorostearates which when saponified with sodium hydroxide solution yield sodium chlorostearates. Dichlorostearic acids (and other chloro-acids as the case may be) are then obtained by acidifying the aqueous soap solution with sulfuric acid. The dichlorostearic acids are then washed and separated. To facilitate washing and separation, an extract may be obtained from an aqueous solution by means of a low boiling solvent (e. g. petroleum naphtha) having selective solvent properties for the chlorostearic acids. As an alternative, I may extract the aqueous mixture with a portion of the lubricating oil eventually to be used. In this event the lubricating oil solution is decanted and allowed to stand at 175° F. to 200° F. until practically all of the water settles.

Chlorinated unsaturated acids.—For the preparation of unsaturated chloro-fatty acids, for example, chloro-oleic acid, operations are carried at lower temperatures than those given for the chlorination of saturated acids, for example 100° F. to 150° F. preferably in the absence of light. Generally the chlorination will be controlled so as to avoid substitution and to aid addition at the double bond, but some substitution may be tolerated. Chlorination of course is to be controlled so as to give the desired percentage increase in weight or chlorine content as well as a low iodine number on the chlorinated product.

PRODUCTION OF SOAPS OF CHLORO-FATTY ACIDS

Considering the production of soaps of chloro-fatty acids of this invention, the method of manufacture here also will be indicated with respect to calcium soaps of the chlorostearic acids, which may be produced either by direct neutralization or by double decomposition of water-soluble soaps.

Direct neutralization.—In preparing the soaps by direct neutralization, either a concentrate may be first produced for eventual blending with an oil or the blended oil may be obtained directly in one operation. In either case neutralization is effected with calcium oxide or hydroxide, preferably the hydroxide which has a more extended form, such materials preferably being employed as a fine powder.

In producing the concentrate the required amount of chlorinated acid is simply dissolved in lubricating oil and the powdered calcium oxide or hydroxide added in an amount equivalent to, slightly less than or greater than that required to neutralize the acids. The addition of a small amount of water (20% to 100% of the weight of the lime) appears to aid in the neutralization. This mixture is stirred and heated to an elevated temperature, preferably to about 325° F. to 350° F. although lower temperatures can sometimes be used, especially where the mixture is subjected to vacuum which aids in removing water after the neutralization is completed. This heating is sufficient to insure complete reaction between the alkali and the acids, and to remove water which would otherwise cause clouding or gelling on cooling, and to otherwise stabilize the mixture. It is desirable to use very pure lime where stearic acids are being employed, the presence of magnesium in the lime being highly objectionable from a clouding standpoint. It has been found preferable to use an excess of lime, particularly when the soap concentration is not too high, and subsequently to heat with agitation to effect neutralization and dehydration and to filter or centrifuge to remove excessive lime or other solid materials. The addition of 0.25% to 1.0% of a refined diatomaceous earth (such as that known on the market as "super-cel") before or during dehydration aids in filtering the concentrate. The production of concentrate is usually carried out in batch.

Dehydration.—It is essential to dehydrate the soap thoroughly, and I have found that this may be accomplished by heating the concentrate or solution with agitation at 325° F. or higher up to a maximum of about 380° F. until all foaming has ceased and the foam is broken. Before this condition is reached, a thickening or gelling is usually experienced and a sample drawn from the kettle and cooled will set to a stiff gel. When the heating and agitation have been continued sufficiently to effect the desired degree of dehydration, a sample drawn from the kettle will remain fluid though viscous on cooling with agitation. The foregoing criteria are used in determining when the batch is ready for clarification as by filtering first through a Sweetland type filter and then through a blotter press. To aid in maintaining a fluid condition after it has cooled, the filtered concentrate may be agitated or "worked" during or after cooling. The concentrate should be stored out of contact with moisture because of the hygroscopic nature of the soaps. Dehydration is to be as complete as possible and the water content preferably is less than about 0.25%.

In dehydrating the soap concentrate, it is usually preferable to use the highest temperature convenient, taking care to avoid the access of air, but if the temperature is carried too high, as for example in excess of 360° F. in the case of concentrated mixtures of calcium dichlorostearate, undesirable decomposition or polymerization reactions begin to occur. The tendency toward decomposition appears to be greater with the more concentrated mixtures.

By this procedure a concentrate containing as much as 45% soap can be manufactured. It will have an acid number of about 4 to 10 which upon dilution to a 1% to 2% concentration in oil will give an acid number in the product of about 0.15 to 0.4.

Soap in situ.—In producing a blended oil in one operation (production of soap in situ) by the direct neutralization method, the amount of acid corresponding to the desired final soap content is added to the lubricating oil to be modified. A small amount of filter aid such as 0.25% to 1.0% of refined diatomaceous earth (such as said "super-cel") may be added depending upon the choice of subsequent operations. Powdered calcium oxide or hydroxide (of which 90% preferably passes a 200 mesh screen) together with 20% to 100% as much water based on the lime, or a slurry of the calcium hydroxide in water, is added in an amount corresponding to the chemical equivalent of the acids. The amount of water added is held to a minimum on account of the problem of foaming during later heating, but the use of some water appears to aid in the neutralization of the acids. This mixture is then passed through a tubular heater or the like, as is commonly done in contact clay treating of lubricating oils, although the heating and dehydration may be done in batch. The temperature is raised to between about 325° F. and 375° F. and the oil is discharged into a surge or flash drum where the water is eliminated in the form of vapor. Vacuum or stripping with an inert gas may be used to aid the removal of water. The oil is then passed through either a centrifuge or a filter to remove undesirable material. In some instances it has been found possible to omit clarification of the mixture from the surge drum by reason of good settling of undissolved materials at that point.

While the use of lime equivalent to the acid requirements may be satisfactory, it is ordinarily preferable to use an excess of the lime between about 10% and 100% excess, the filter aid mentioned being used in this instance also. This filter aid, which preferably is an inert material such as the purified diatomaceous earth above mentioned, should not in general contain large amounts of adsorbent clay or bleaching agent, because the highly adsorptive clays have a tendency to remove the soap and thereby decrease the effectiveness of the product. However a very small amount of bleaching clay may sometimes be employed to improve color without serious loss of soap therefrom.

Soap production by double decomposition.—In addition to the direct neutralization above described, the soaps may be prepared by double decomposition of the water-soluble soaps in solution by means of calcium chloride or nitrate or like water-soluble calcium salts. Such water-soluble soaps may be sodium chloro-soaps such as above described as being prepared from the

chlorinated esters, or of course they may be prepared by direct neutralization of chloro-stearic or other indicated acids which have been produced by direct chlorination of such acids. Solid calcium chloride or nitrate or solutions thereof may be used. The operation consists merely in adding the calcium salt or its solution to the soap solution and agitating to effect adequate mixture, whereupon the soap is precipitated, filtered, and washed at temperatures below the melting or sintering point. The soap is then air dried at not over 125° F. Vacuum drying may be used advantageously at these temperatures. The object of restricting the temperature is to avoid sintering. Should it not be desired to handle the soap as a dried solid after its precipitation by double decomposition and recovery, a portion of lubricating oil may be added before, during or after the addition of the water-soluble calcium salt above mentioned, the temperature being now maintained above the melting point of the soap, for example at 180° F. In this mixture the soap precipitates and is gathered into a magma or viscous mass which can be washed with hot water by decantation. This procedure avoids filtration and air drying. After the resultant pulp is washed until practically free from inorganic salts (e. g. calcium chloride), additional small proportions of oil may be added if desired. This pulp is then dried by heating with closed steam (such as in a steam jacketed grease kettle) to bring it to a temperature between about 300° F. and 350° F. while being agitated. This operation yields a concentrate which after heating and agitation is a viscous, flowable, non-cheesy fluid at ordinary temperatures. By restricting the oil content this concentrate may be made to contain about 45% of the soap or by increasing the oil content it may be made to contain as little soap as desired. More than about 45% soap renders the concentrate stiff and difficultly flowable and therefore awkward to handle. Such concentrates are readily miscible with lubricating oil in all proportions.

Blending Final Products

The blending of a soap concentrate with a lubricating oil of such type as has been hereinabove indicated, may be carried out at any temperature at which the components are sufficiently fluid to obtain thorough mixing, for example 120° F. to 150° F. However, if dry, solid soap is used, it is desirable to heat after adding the soap to the oil to insure complete dehydration as explained above. In some instances it has been found desirable to subject the finally blended oil to a clarification treatment as by centrifuging or by filtering to remove any haze which might be present from a number of sources, for example contamination from the equipment or from reagents or from the presence of oil-insoluble soaps including unchlorinated calcium stearate or oil-insoluble magnesium soaps. As has been indicated, the presence of magnesium may be eliminated by purification of the lime before use.

Free acidity.—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 in oil. This free acidity usually represents only a small proportion based on the blended oil, the range usually being between about 0.07% and 0.2% (corresponding roughly to acid numbers of about 0.14 to 0.4, i. e. mg. KOH per gram 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 batch of soap which is prone to give excessive increase in viscosity, cloud or sedimentation in the blended oil is usually improved in its blendability by the presence of some free acid. Usually it is permissible and convenient for the free acid to belong to the same class as the acids used in forming the soap. However other acids such as unchlorinated oleic acid are sometimes conveniently usable. Furthermore, it has been observed that simply heating and holding a cloudy concentrate or diluted blend at an elevated temperature, for a period of time, for example at about 325° F. for one hour, improves the compatibility of the soap in the oil upon cooling, and subsequent titrations usually indicate an increase in acid number under these conditions without the necessity for any other adjustment or exercise of care to insure an acid content. It is preferable, however, to avoid excessively high free acid contents because of the possibility of encountering corrosion with certain engine materials such as bronze bearings or bushings.

Controlling acidity — re-neutralization.—Organic bases such as triethanolamine can be employed in some cases as an aid in controlling acidity. This use will be understood from the following example. A batch of soap concentrate containing approximately 20% calcium dichlorostearate was found to give a blended oil of 0.7 acid number when diluted to a soap content of 1.3%. This soap concentrate had been produced by heating a mixture of mineral oil, chloro-acids (20% chlorine content) and a slight excess of lime to 325° F. with agitation and holding at 325° F. to 340° F. until dehydration was complete. The dehydrated concentrate containing 0.5% refined diatomaceous earth "Super-cel") was filtered giving the 20% concentrate referred to above. For the purpose of reducing the acid number obtained on blending, a portion of the concentrate was retreated with lime and said earth and a definite improvement was obtained as shown by an acid number of 0.4 on blending to 1.3% soap content. However, to obtain a still further reduction in acid number, another portion of the concentrate was retreated with the same amount of lime and earth as used in the last operation but 0.5% triethanolamine was added when the concentrate was at 250° F. during the heating up to 325° F. After complete dehydration, the mixture was filtered, giving a product which was fluid on cooling and yet which gave an acid number of only 0.2 on blending to 1.3% soap content.

In other instances small amounts of concentrated aqueous solutions of sodium hydroxide and potassium hydroxide have been used alone and in conjunction with additional lime in the reneutralization to obtain unusually low acid numbers of the order of 0.05 on the finished engine lubricant containing 1.3% total soaps. An oil reneutralized with concentrated KOH, for example, was found to be especially non-corrosive to bronze wrist pin and babbit crank shaft bearings. The use of alcoholic potassium hydroxide or sodium or potassium alcoholates such as potassium methylate and ethylate is practical and has the advantage of reducing foaming difficulties attendant upon the last stages of dehydration as explained elsewhere. In carrying out the reneutralization with solution of alkali hydroxide, it is often more feasible, espe-

cially in batch operations, to cool the lime-neutralized mix to below the boiling point of water, or alcohol as the case may be, before adding the solution of alkali. Also the unreacted lime and other solids from the previous neutralization may or may not have been filtered off before the alkali for the re-neutralization is added. If the alkali is added after filtering off unreacted lime, etc., it is advisable to add an additional amount of "super-cel," reheat and refilter.

Where the acid number in a soap-oil concentrate containing considerable soap, e. g. 40%, is brought below about 1.5, the tendency is for the concentrate to become cheesy. Here the filtering may be left until the blending operation when the final blend is heated to effect final dehydration and is finally filtered to remove unreacted solids.

Thus, the control of acidity by reducing the acid number, where too high, by re-neutralization as above indicated, may be accomplished by retreatment with additional quantities of the same base as originally employed such as the calcium hydroxide, or by treatment with other bases such as NaOH or KOH with or without clay or the earth above mentioned, or ammonium carbonate, or organic bases such as the mentioned triethanolamine, or monoethanolamine, triethylene tetramine, triamylamine, morpholine and the like. Where the base used for reneutralization is different from that originally used, soap mixtures are of course obtained. Very desirable results have been obtained with the mixture heretofore mentioned containing 1% calcium chlorostearates and 0.3% triethanolamine chlorostearates, which was produced through the above described re-neutralization. A very desirable and apparently preferential maximum acid number of about 0.2 may be obtained by such procedures as well as the above indicated unusually low acid number of only 0.05. As in the original neutralization, the use of a small amount of water in the re-neutralization is helpful.

PRODUCTS

A typical oil produced for Diesel engine lubrication consisted of 1.3% calcium chlorostearates and 98.7% Western type naphthenic base oil of

Gravity	20.8° A. P. I.
Viscosity	511 seconds Saybolt Universal at 100° F.; 54.5 seconds at 210° F.
Pour point	Flows at −10° F.
Flash C. O. C.	380° F.
Ash	Nil
Color	3 N. P. A.
Acid number	0.03
Carbon residue	0.10

The calcium chlorostearates contained 18.5% chlorine based on the acid which was representative of dichlorostearate predominantly. The resultant blend possessed the following characteristics:

Gravity	20.6° A. P. I.
Viscosity	550 seconds at 100° F.; 55 seconds at 210° F.
Pour point	Flows at −10° F.
Flash C. O. C.	380° F.
Ash	0.13
Color	4 N. P. A.
Acid number	0.18
Carbon residue	0.32

In addition to chlorinated calcium stearates as above indicated other suitable oil-soluble soaps may be employed such as aluminum dichloroleate and aluminum dichlorostearate. However, I have found that for most purposes magnesium soaps of such chlorinated acids are not desirable because of their strong tendency to cloud. In addition to the ordinary elimination of magnesium, it is also desirable to avoid a very large proportion of unchlorinated stearic acid for the reason that neither the stearic acid itself nor calcium stearate therefrom is sufficiently soluble in or compatible with the oil. However, as stated above, the chloro-soaps have a marked solubilizing action on unchlorinated soaps and it therefore usually is unecessary to eliminate all unchlorinated acids. The exact proportion of unchlorinated acids or soaps therefrom that can be tolerated depends on both the acid and the oil being treated. In general, the more naphthenic the oil, the more unchlorinated acid can be tolerated, whereas with a highly paraffinic oil, it has been found preferable in the case of stearic acids, to purify the chloro-acids to a point of practically complete elimination of unchlorinated stearic acid, as by refining the chloro-acids by cold pressing to a pour point of −25° F.

Also, certain soap mixtures are very desirable, especially a mixture of the indicated calcium chlorostearates and calcium phenyl stearate in proportions ranging for example from one part of one of the soaps to three parts of the other of the two soaps, the soap being used in the percentage range heretofore indicated between about 1% and about 2% combined soap in the average Diesel engine lubricating oil. Also, the above indicated mixtures obtained by re-neutralization such as calcium chlorostearates with smaller proportions of triethanolamine chlorostearates (such as dichlorostearates) and similar soaps are valuable. My invention includes also such soap mixtures in oil regardless of the method of production of the soaps.

Other soaps.—Again, soaps of other chlorinated fatty acids having a minimum of about 14 carbons to insure a sufficiently high molecular weight and boiling point may be employed. Corresponding soaps of chlorinated synthetic petroleum acids likewise may be employed. These acids themselves are well known on the market, and are frequently produced by oxidation, catalytically and otherwise, of paraffinic petroleum products, oxidation being a convenient means for the formation of the acids. These acids are recovered by converting into water-soluble alkali soaps and subsequently cracking out by the use of strong mineral acids to yield the purified acids. These procedures are generally well understood and need not be here described. These acids may be more or less readily chlorinated or otherwise halogenated by passage of the halogen gas through the liquid acids to effect the desired substitution and/or addition, followed by removal of HCl and excess Cl_2. The soaps of such halogenated acids are then readily formed by reaction with suitable metal salts, hydroxides or oxides in the same way that fatty acid soaps are formed. Usually the synthetic petroleum acids recovered as indicated above contain also certain other types of compounds such as ketones and esters, and the presence of these other types of molecular structures has been found to be beneficial generally speaking rather than detrimental. In fact experience has shown that the

presence, as such, of the ester-ketonic products obtained during the oxidation of paraffinic hydrocarbons or produced by esterification of synthetic petroleum acids with methyl or ethyl alcohol is often desirable from the standpoint of oiliness and maintaining a tightly adsorbed layer of non-corrosive material which protects against corrosion of the metal from water, combustion products, decomposition products and the like.

With respect to the synthetic petroleum acids, paraffin acids and the like such as produced by oxidation as herein mentioned, as distinguished from naphthenic acids, attention is called to the fact that these acids are of different character from naphthenic acids and present a vastly greater degree of oiliness properties than do the naphthenic acids and are in most instances to be preferred to naphthenic acids or any other naturally occurring petroleum acid such as obtained from petroleum distillates. The synthetic petroleum and paraffin acids mentioned may be produced by oxidation as well understood in the art or otherwise. The esters of the synthetic petroleum acids are also valuable adjuncts to oil-soluble soaps as explained above. For example the performance of an oil containing 1.25% of calcium dichlorostearate was improved by the addition of 1% of methylated ester obtained from oxidized paraffin wax.

In addition to the indicated metal soaps of various halogenated fatty acids such as oleic, linoleic, stearic, palmitic and the like, and the indicated soaps of halogenated naphthenic acids and halogenated synthetic petroleum acid, I may also use corresponding oil-soluble sulfurized or phosphorous-bearing soaps of such acids of sufficiently high molecular weight as herein indicated. Also, I contemplate the use of special soaps, such as a lead soap of highly chlorinated organic acids, particularly naphthenic acids, as components in extreme pressure gear oils and the like. Thus, the oil-soluble lead soaps of the chlorinated or otherwise halogenated naphthenic acids, corresponding sulfurized acids, and halogenated and sulfurized lard oils and fatty acids, and the like are included. These acids should contain at least ten carbon atoms per molecule. Such lead soaps may be used alone or in conjunction with other halogenated or sulfurized soaps herein disclosed or with oiliness agents of the oxygenated type such as esters, ketone, etc., produced from oxidized petroleum fractions.

Organic bases.—Similarly, I may use organic bases in preparing soaps for the use of the present invention. Such bases are represented by triethanolamine, quinoline bases, nitrogen bases from petroleum and the like. Where the triethanolamine soap is to be used as one of the components of a two-component additive material, the acids would not generally contain an oiliness element such as chlorine, sulfur or the like. Such acids may be naphthenic acids, fatty acids containing a minimum of about 14 carbon atoms, synthetic petroleum acids as from oxidation of paraffin waxes and refined petroleum oils and all other types of acids herein mentioned. When the organic base soap, such as a triethanolamine soap, is to be used as a single component additive, then the acid radical will contain the oiliness agent such as chlorine, sulfur, phosphorus or other suitable substituent. Soaps of this character will be used in percentages similar to those employed with other soaps, or in smaller percentages when used in conjunction with other oil-soluble metal soaps.

Soaps in general.—In all aspects of the present invention, it will of course be obvious that in the case of chlorinated or sulfurized or similar materials either the acids employed may first be chlorinated or otherwise treated, or the soaps after their formation may be so chlorinated, sulfurized, or otherwise modified, and the materials produced by both methods are intended to be included when acids and soaps are mentioned herein.

Soaps of the indicated nature when added to lubricating oils are stable in use, and when employed in the indicated proportions do not appreciably affect the fluidity of the oils for lubrication purposes. The amount of soap to be added to the oil, as is evident from the above disclosure, is that quantity necessary to effectively avoid substantial deposit of gummy, resinous and varnish-like materials whereby to overcome ring and valve sticking in internal combustion engines especially engines of the Diesel type, and also in high output aviation engines. At the same time tendencies in fuel used in the engines to deposit similar or other gummy resinous varnish-like constituents which tend to cause ring valve sticking, are likewise overcome by the use of such amount of the indicated type of soap. As has been indicated, this amount is ordinarily in the order of about 1%. Besides an ordinary range between about 1% and 2% as previously indicated, there may be instances where as little as 0.25% may be used, and on the other hand, larger amounts extending up to possibly as high as 3% may be desirable under some conditions. In other words, varying conditions can possibly require wider ranges.

Multi-component materials.—According to another form of the invention, I have found it practicable to use a two-component additive material, one of which is a non-halogenated or non-sulfurized soap for the purpose of prevention of deposition of gums and resins and the like, and the other of which is an oiliness constituent which imparts high load carrying capacity. Whereas, in the case of a single component material, calcium dichlorostearate for example, both the oiliness element and the element for overcoming deposition of gums and resins are contained in one compound, in this modification of the invention the soap which largely overcomes deposition of gums and resins does not contain combined therein an agent for improving oiliness and film strength, such as sulfur, a halogen, phosphorous, or the like, but the soap is employed in conjunction with a second component which is halogenated, sulfurized or phosphorized of which methyl dichlorostearate is a good example, such second agent imparting the desired increased load carrying capacity. For example, I may employ approximately 1% to 1.5% of an oil-soluble calcium soap of palm oil acids, oleic acid, phenylstearic acid or the like, or other disclosed acid, together with about 0.5% to 1.0% of methyl dichlorostearate to increase film strength and load carrying capacity. Other oiliness or film strength agents of this general type may be substituted such as those produced from ethyl, amyl or other alcohols and oleic, palmitic, phenyl stearic and other acids, the agent containing chlorine. In addition to halogenated ester types, I may employ other types of oiliness or film strength agents, such as chlorinated naphthalene, chlorinated diphenyl oxide, chlorinated paraffin, sul-

furized lard oil, chlorinated or sulfurized jojoba oil (which is a vegetable oil which readily takes up either small quantities of sulfur or large quantities as high as 25% sulfur, without turning black), sulfurized fatty acid esters, tricresyl phosphate and kindred phosphorous compounds; and oxygenated compounds of the ester, ketonic or aldehydic types such as those obtained from oxidized paraffinic petroleum fractions, as such or when chlorinated. In this manner the oiliness element such as chlorine, sulfur, phosphorous, or oxygen, is obtained through the medium of an agent other than the soap.

Also, in addition to the type of soaps containing a film strength agent, such as calcium dichlorostearate or triethanolamine dichlorostearate (or a mixture), I may use therewith a second material not a soap such as those non-soap materials above mentioned for imparting oiliness characteristics, but more especially materials of which esters of the above mentioned synthetic petroleum acids obtained by oxidation of paraffinic materials are representative; for example the methyl esters of such synthetic petroleum acids in particular, and also ethyl and amyl esters and the like. Such second material may or may not be chlorinated. In such blends only the soap needs to be confined within the indicated limits of about 1% to 2%, but the other additive would ordinarily not exceed an additional 1% or thereabouts. Also, my invention includes the use of these chlorinated esters of synthetic petroleum acids obtained by oxidation, as oiliness agents in lubricating oil in amounts between limits of about 0.25% to 3% and with or without soaps or other types of addition agents.

Mineral lubricating oils to be used in practicing this invention are normally of the ordinary S. A. E. grades employed for engine lubrication, and more particularly the S. A. E. 20, 30 and 40 grades, but the invention is not necessarily limited thereto.

Ordinarily, and except where otherwise indicated, the term "dichlorostearate" or "dichlorostearic acid" or equivalent term is intended to include also the soap or acid obtained by saturation of oleic acid with chlorine, the two products appearing to be equally valuable, the only difference being that the chlorines appear to enter at different places in the chain.

In stating that the indicated proportions of soaps employed in lubricating oils (i. e. in the order of about 1% to 2%) do not appreciably affect the fluidity of the oils, this refers to a viscosity increase of less than one S. A. E. grade or an increase of not over about four seconds Saybolt Universal at 210° F.

When the term "complete dehydration" is used herein it means that degree which renders the concentrate flowable as herein described and perhaps reduces the water content to as little as 0.25% or less.

Where the term "calcium oxide" is used in referring to the base material employed for soap production, it is intended to include both the anhydrous calcium oxide as such or the hydrated calcium oxide (hydroxide), except where otherwise indicated.

While the invention has been indicated as particularly applicable to mineral lubricating oils, it may also be extended to fatty lubricating oils and the like.

It is to be understood that the above disclosures are furnished as being illustrative of the present invention, and that they are not to be taken as limiting beyond the requirements of the prior art and as indicated by the appended claims.

I claim:

1. A lubricant comprising at least about 97% of mineral lubricating oil and between about 1% and 2% of oil-soluble soap constituent of organic acid containing ten or more carbon atoms and including a film-strength increasing constituent in a class consisting of halogens, sulphur and phosphorous, said soap not materially increasing the viscosity of the oil and possessing detergent properties for gums and the like formed in internal combustion engines, the soap being substantially anhydrous.

2. A Diesel engine lubricating oil comprising a mineral lubricating oil and oil-soluble metal soap constituent of organic acid containing at least ten carbon atoms and including a halogen film-strength improving constituent, the additive soap material being in the order of 1% to 2% and sufficient only approximately to overcome ring sticking and formation of gummy and varnish-like bodies but insufficient to materially increase the viscosity of the mineral lubricating oil, the soap being substantially anhydrous and the oil containing a small proportion of a common solvent for the soap and oil.

3. A Diesel engine lubricating oil comprising mineral lubricating oil containing between about 1% and about 2% of oil-soluble metal soap of chlorinated fatty acid having a chlorine content between about 15% and 25%, being substantially anhydrous and containing a small proportion of unsaponified fatty acid, whereby the soap is freely dissolved in the oil and without material increase in viscosity.

4. A Diesel engine oil according to claim 3 wherein the chlorine content corresponds generally to a dichloro soap.

5. A severe service engine lubricating oil comprising a mineral lubricating oil containing between about 0.8% and about 2% of calcium soap of chlorinated fatty acid having ten or more carbon atoms to the molecule and having a chlorine content between about 15% and 25%, the product being approximately anhydrous and containing a small proportion of free saponifiable organic acid as a solubilizing agent and being free from substantial increase in viscosity over the base oil.

6. A lubricating oil comprising mineral lubricating oil and between about 0.8% and about 2% of oil-soluble soap of fatty acid containing at least ten carbon atoms and having a chlorine content between about 17% and 21% based on the acid, the product being approximately anhydrous and containing a small proportion of free saponifiable organic acid as a solubilizing agent and being free from substantial increase in viscosity over the base oil.

7. A Diesel engine lubricating oil comprising mineral lubricating oil and between about 1% and about 2% of calcium soap of chlorinated organic acid containing ten or more carbon atoms, the soap possessing a chlorine content representative of a predominating proportion of calcium di-chloro soaps, the product being approximately anhydrous and containing a small proportion of free saponifiable organic acid as a solubilizing agent and being free from substantial increase in viscosity over the base oil.

8. A normally flowable substantially anhydrous lubricant comprising as principle ingre-

dients mineral lubricating oil and at least about 0.8% of oil-soluble soap of organic acid of the class consisting of halogenated, sulphurized and phosphorized synthetic petroleum and fatty acids containing ten or more carbon atoms.

9. A Diesel engine lubricating oil comprising mineral lubricating oil having naphthenic base characteristics containing a small quantity in the order of about 1% to 2% of substantially anhydrous oil-soluble metal soap of chlorinated organic acids containing ten or more carbon atoms and a smaller proportion of unsaponified organic acid to insure solution of the soap in the oil.

10. A Diesel engine lubricating oil containing a small quantity between about 0.8% and 2% of substantially anhydrous calcium chlorostearate containing chlorine corresponding approximately to the dichloro-stearate, without substantial increase in the viscosity of the original lubricating oil.

11. A Diesel engine lubricating oil comprising a naphthenic base mineral lubricating oil and between about 0.8% and 2% oil-soluble substantially anhydrous calcium chloro-stearates, the oil being freely liquid without substantial increase in viscosity over the original lubricating oil.

12. A mineral lubricating oil especially adapted for use in severe service internal combustion engines comprising a mixture freely liquid at normal temperatures of a naphthenic base mineral lubricating oil and between about 1% and 3% of an oil-soluble calcium soap of a chlorinated organic acid containing at least ten carbon atoms, the soaps containing between about 10% and about 40% of chlorine based on the acid, the resultant product being substantially anhydrous and having the character of overcoming accumulation of resin and varnish-like materials upon piston rings in internal combustion engines without appreciable increase in the viscosity of the original base oil.

13. An oil according to claim 12 having free small organic acid content to insure solution of the soap in the oil and freedom from substantial viscosity increase.

14. A lubricant comprising mineral lubricating oil and a substantially anhydrous mixture of calcium phenyl-stearate and calcium chlorostearates corresponding generally with calcium dichlorostearate.

15. A lubricating oil containing between about 1%-and 2% of a mixture of calcium chlorostearates containing between about 15% and 25% chlorine, and triethanolamine chlorostearate.

16. A lubricating oil containing between about 1% and 2% of a mixture of calcium chlorostearates containing between about 15% and 25% chlorine, and potassium chlorostearate.

17. A substantially anhydrous lubricant comprising mineral lubricating oil, oil-soluble metal soap of chlorinated fatty acid having at least ten carbon atoms, and lead soap of chlorinated naphthenic acid, the combined soap content being at least about 1% based on the mineral oil.

18. A substantially anhydrous lubricating oil comprising mineral lubricating oil, oil-soluble lead soap of chlorinated organic acid of the class consisting of synthetic petroleum acids, naphthenic acids and fatty acids containing at least ten carbon atoms in the molecule, and oil-soluble soap, other than said lead soap, of chlorinated organic acid from the class consisting of synthetic petroleum acids and fatty acids containing at least ten carbon atoms in the molecule, the combined soap content amounting to at least about 1% of the oil.

19. A substantially anhydrous Diesel engine lubricating oil comprising as primary constituents a naphthenic base mineral lubricating oil and between about 1% to 2% of oil-soluble metal soap of chlorinated organic acid from a class consisting of synthetic petroleum acids containing ten or more carbon atoms to the molecule and fatty acids containing at least ten carbon atoms to the molecule.

20. A lubricating oil according to claim 32 containing between about 0.8% and about 2% of calcium soap of the acid.

21. A substantially anhydrous lubricating oil for heavy service internal combustion engines comprising a mineral lubricating oil having good solvent power for soaps and containing between about 1% and about 2% combined of oil-insoluble soap of organic acid containing at least ten carbon atoms and oil-soluble soap of organic acid containing at least ten carbon atoms and also containing chlorine in sufficient quantity to render the soap oil-soluble, said oil-soluble soap being in excess of the oil-insoluble soap and exerting a solubilizing action upon said oil-insoluble soap.

22. A viscous concentrate for the addition to lubricating oils comprising a substantially anhydrous mixture of mineral lubricating oil and between about 10% to 45% of oil-soluble soap of chlorinated fatty acid containing at least ten carbon atoms, the soap containing between about 10% and 40% of chlorine based on the acid, the concentrate being flowable at normal room temperature.

23. A method for preparing lubricating concentrates comprising mineral lubricating oil and oil-soluble soap wherein the soap contains between about 10% and 40% chlorine, said method comprising adding chlorinated fatty acids containing at least 10 carbon atoms to mineral lubricating oil, adding a base to the mixture, heating and agitating to effect neutralization of the mixture with a residual acid number in excess of 0.2, filtering, and re-neutralizing the mixture with base to reduce the acid number to a maximum less than approximately 0.2, and filtering.

24. A method according to claim 23 wherein the first base is calcium oxide and the second base is an ethanolamine.

25. A method according to claim 27 wherein the first base is calcium oxide and the second base is potassium hydroxide or alcoholate.

26. A method of preparing lubricating oils comprising chlorinating normally solid fatty acids to effect a mixture of relatively heavily chlorinated fatty acids and lightly chlorinated or unchlorinated materials, chilling the mixture to precipitate unchlorinated and lightly chlorinated materials, cold pressing the chilled mixture to recover liquid more heavily chlorinated fatty acids, saponifying said normally liquid chlorinated fatty acids to yield oil-soluble soaps, effecting solution of the resultant soaps in mineral lubricating oils and effecting dehydration of the mass.

27. A method for the preparation of lubricating oils comprising chlorinating material containing a stearic acid radical to produce chlorinated stearic acids corresponding in chlorine content to dichlorostearic acid, recovering such stearic acids, effecting solution of such stearic acids in lubricating oil, adding calcium oxide,

heating to effect reaction to produce calcium chloro-stearates and substantially dehydrate the solution, and filtering out undissolved materials.

28. A lubricating oil for internal combustion engines comprising mineral lubricating oil containing between about 1% and 2% calcium soap of chlorinated fatty acids containing at least ten carbon atoms to the molecule and chlorine representative of a preponderance of dichloro acids, the composition being substantially free from water and water-soluble salts, and containing a small proportion of free saponifiable organic acid as a solubilizing agent.

29. A dehydrated soap concentrate comprising mineral lubricating oil containing oil-soluble calcium soap of chlorinated fatty acids having at least ten carbon atoms to the molecule and containing chlorine representative of a preponderance of dichloro acids, the composition being substantially free from calcium chloride.

30. A method for producing lubricating oils which comprises forming a calcium soap of chlorinated fatty acids containing at least ten carbon atoms to the molecule, supplying a proportion of lubricating oil to the soap, washing the soap-oil mixture until the mixture is substantially free from metal chloride, and dehydrating the mixture.

31. A method for the production of lubricating oil concentrates comprising reacting chlorinated fatty acids containing at least ten carbon atoms to the molecule with a calcium compound to produce calcium soap in the presence of a proportion of mineral lubricating oil, filtering the soap-oil mixture, washing to remove water-soluble materials including calcium chloride, dehydrating the resultant soap-oil concentrate, and combining the washed, dehydrated concentrate substantially free from calcium chloride with additional mineral lubricating oil.

32. A lubricating oil which is freely liquid at ordinary temperatures comprising a mineral lubricating oil containing more than about 0.8% of an oil-soluble metal soap of a saponifiable organic acid containing at least 10 carbon atoms to the molecule in chemical combination with a film strength increasing agent of the class of the halogens, sulfur and phosphorous and containing sufficient unsaponified organic acid to obtain free dispersion of the soap and render the soap mixture freely fluid, the oil product being substantially anhydrous and possessing substantially the same viscosity as the original mineral lubricating oil.

33. An oil according to claim 32 wherein the soap is an alkaline earth metal soap containing chlorine corresponding roughly to the dichloro soap.

34. An oil according to claim 32 wherein the soap is a calcium chloro fatty acid soap containing chlorine corresponding roughly to the dichloro soap.

35. A lubricating oil which is normally freely liquid comprising mineral lubricating oil and at least about one percent of calcium chloro fatty acid soap containing chlorine corresponding generally with the dichloro soap, the soap being almost completely anhydrous and freely soluble in the oil without imparting substantial viscosity increase or grease-like characteristics to the original lubricating oil.

36. A lubricating oil according to claim 35 wherein the mineral oil is a naphthenic base oil.

37. A lubricating oil according to claim 35 wherein the product contains in the order of 0.07% to 0.2% of unsaponified organic acid.

ULRIC B. BRAY.

CERTIFICATE OF CORRECTION.

Patent No. 2,225,366. December 17, 1940.

ULRIC B. BRAY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 9, second column, line 27, after "ring" insert --and--; page 11, second column, line 53, claim 25, for the claim reference numeral "27" read --23--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of April, A. D. 1941.

Henry Van Arsdale,

(Seal) Acting Commissioner of Patents.