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MANUFACTURE OF LUBRICATING OILS

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This invention relates to compounded lubricating oils containing oxidation and corrosion inhibitors and more specifically to lubricating oils containing metal salts of petroleum sulphonic acids and primarily intended for use in the lubrication of internal combustion engines.

It is now common in the manufacture of lubricating oils intended for heavy duty service, such as, for example, the so-called "high speed" Diesel engines, to employ addition agents for the purpose of improving the oil in one or more of the following characteristics:

(1) Resistance to oxidation and sludge formation.

(2) Cleanliness of engine, and resistance to piston ring sticking.

(3) Oiliness, or resistance to scoring or scuffing.

(4) Resistance to corrosion of the working parts of the engine, particularly to alloy bearings of the copper-lead type.

The above characteristics are desirable in lubricating oils subjected to less severe service and, consequently, it is becoming common to employ similar addition agents in oils intended for general service.

A myriad of compounds and combinations of compounds have been proposed for improving mineral lubricating oils in one or more of the above manners. In some cases the additive has improved the oil with respect to one feature, but has been detrimental in respect to another. This has resulted in the trial of various combinations of additives for securing the desired result. Polyvalent metal salts of sulphonic acids derived from petroleum, particularly those of the alkaline earth metals, have been found to be particularly useful in supplying the desired properties to lubricating oils to a great degree. However, recently the power output and efficiency of automotive engines has been substantially increased as a result of higher speeds and higher compression pressures, as a result of which oils compounded with metal sulphonates, as customarily manufactured, have been unable to supply the desired characteristics to the desired degree. In accordance with the present invention, it has been found that, by proper processing, oils containing metal sulphonates can be prepared with greatly enhanced ability to provide for engine cleanliness and with markedly increased freedom from corrosion.

In the conventional method of manufacturing metal sulphonates for use as additives in lubricating oils, a raw petroleum distillate is treated with

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strong sulphuric acid whereby the most readily sulphonated constituents are converted into sulphonic acids, part of which remain in the oil. These oil-soluble acids are then removed from the oil by treatment with aqueous sodium hydroxide or other alkali whereby they are converted into water-soluble alkali metal sulphonic salts which dissolve in the aqueous caustic soda and leave a refined hydrocarbon oil. The process to this point is conducted primarily for the purpose of refining the hydrocarbon oil, the recovery of the sulphonic salts being entirely secondary. According to general practice, the alkali metal sulphonic salts derived as above are converted into the desired polyvalent metal sulphonate by treatment with a water-soluble inorganic salt of the required metal. The water-insoluble metal sulphonate precipitates from the aqueous solution as a voluminous mass which readily retain appreciable quantities of unreacted sodium sulphonate and other impurities which are very difficult to remove, even by prolonged washing with boiling water. Sodium sulphonate is thus retained as an impurity in the desired metal sulphonate and, when the latter is added to a lubricating oil, has been found to be very detrimental to engine performance inasmuch as the sodium sulphonate promotes sludge formation and is very corrosive to alloy bearings. Furthermore, the contaminating sodium sulphonate imparts to the oil an appreciable affinity for moisture and results in an increased tendency toward rusting of the metal parts of the engine during periods of inoperation.

The presence of the sodium sulphonate impurity may be avoided by preparing the desired polyvalent metal sulphonate from free sulphonic acids which have been extracted from acid treated oils without the use of caustic soda; for example, by the method of preparing sulphonic acids disclosed in U. S. Patent 2,218,174, issued October 15, 1940, to Lazar and Ruedrich.

The presence of the sodium sulphonate impurity also may be avoided by manufacturing the desired metal sulphonate directly in the oil as described by Bergstrom in U. S. Patent 2,270,577. In this procedure a suitable lubricating stock is treated with concentrated or fuming sulphuric acid, thereby producing sulphonic acids dissolved in the oil. After separating the acid sludge, the sulphonic acids are neutralized directly in the oil with oxide or hydroxide of the required polyvalent metal. By following this procedure, the oil is both purified and provided with the additive simultaneously without the necessity of the inter-

mediate production of alkali metal sulphonates.

In preparing oils of greatly enhanced anti-sludging, anti-ring-sticking, and anti-corrosion properties compounded with polyvalent metal salts of petroleum sulphonic acids in accordance with the present invention, it is important to avoid any contamination with alkali metal sulphonate as such contamination will counteract to a large extent the advantages gained by the invention. The invention, therefore, contemplates the use of some such method, or other method which may suggest itself, for preparing polyvalent metal sulphonate free from alkali metal contamination. The above-mentioned method described by Bergstrom is preferred, in some respects, due to the simplicity of manufacturing steps involved.

Hitherto, in the preparation of polyvalent metal sulphonates for use as addition agents in lubricating oils, paraffin base oils have been greatly preferred as the source from which the sulphonic acids are to be derived, regardless of whether the sulphonate is finally to be blended into paraffin base oil, into naphthene base oil, or into a blend of paraffin and naphthene base oils. This is principally because metal sulphonates made from sulphonic acids derived from the sulphonation of naphthene base oils usually exhibit a highly corrosive action toward alloy bearings, especially those of the copper-lead type, particularly after long periods of operation in the engine. Also, oils compounded with metal sulphonates derived from naphthene base oils frequently do not possess the resistance to oxidation commonly exhibited by similar oils compounded with metal sulphonates derived from paraffin base oils. On the other hand, the yield of sulphonic acids from naphthene base oils is, in most cases, about double that obtainable from paraffin base oils except under the most excessive sulphonating conditions. Accordingly, if it were not for the above mentioned disadvantages of metal sulphonates derived from naphthene base oils, such oils would be far more economical as a source of the sulphonic acids, both because of the greater yields obtainable and because of their relative cheapness.

The present invention provides a means whereby naphthene base oils may be properly selected and treated to yield sulphonic acids and polyvalent metal sulphonates at least equal to those derived from paraffin base oils with respect both to resistance to oxidation and freedom from corrosion. As a consequence, greater yields of polyvalent metal sulphonates, for use as addition agents in lubricating oils, have been made possible from relatively inexpensive, and hitherto unsatisfactory, raw material. In a particular form of the invention excellent results are obtained by deriving the sulphonic acids from properly selected and treated mixtures of paraffin and naphthene base oils, all of which is hereinafter set forth.

It is, therefore, an object of the invention to provide lubricating oils containing polyvalent metal sulphonates derived from naphthene base oils and having greatly enhanced ability to maintain engine cleanliness.

Another object is to provide such oils having greatly reduced tendency to corrode alloy bearings.

A further object is to provide a method for obtaining from naphthene base oils polyvalent metal sulphonates superior to those customarily made therefrom.

Other objects will be apparent in the following description.

We have found that, to a great degree, corrosive action is imparted to lubricating oils containing metal sulphonates by the presence of minute quantities of other metal salts, especially those of naphthenic acids and of other acidic substances generally present in oils of naphthenic origin. On sulphonation of naphthenic oils, these acidic substances are only partially removed by the sulphuric acid treatment, or they may even undergo sulphonation themselves. Consequently, an appreciable quantity remains in the oil in their original form or as sulphonated acids and thus contaminate the sulphonic acids formed. Whether the sulphonic acids are converted to polyvalent metal sulphonate directly in the oil or whether they are first extracted from the sulphonated oil and subsequently converted to polyvalent metal sulphonate, the acidic impurities or their reaction products will simultaneously be converted to their corresponding metal salt which will contaminate the metal sulphonate and make the same corrosive to alloy bearings. By carefully removing these acidic impurities from naphthene base oils prior to sulphonation it is found that such oils, upon subsequent sulphonation, yield oil soluble sulphonic acids which may be converted to polyvalent metal sulphonate having excellent freedom from corrosion.

Further, we have found that polyvalent metal sulphonates derived from the sulphonation of the lower boiling naphthenic base oils do not provide as great a degree of freedom from ring-sticking and resistance to oxidation as provided by metal sulphonates derived from the sulphonation of paraffin base oils or the higher boiling naphthenic base oils. On the other hand, alkaline earth metal sulphonates made from sulphonic acids derived from the sulphonation of high molecular weight oils exhibit an ability to maintain engine cleanliness to a greater degree than metal sulphonates derived from low molecular weight oils.

The advantages obtainable by utilizing the above discoveries are illustrated in the following table which shows the results of comparative runs made on a single cylinder Diesel engine and a four cylinder Diesel engine, both having copper-lead bearings, using an S. A. E. 30 blend of naphthene and paraffin base oil containing 3% of calcium sulphonate prepared in various manners.

Run A was for a duration of 240 hours in the four cylinder engine using an oil compounded with calcium sulphonate derived from the sulphonation of a 1000 sec. S. U. @ 100° F. naphthene base oil from which naphthenic acids were not removed.

Run B was for a duration of 240 hours in the four cylinder engine using an oil compounded with calcium sulphonate derived from the sulphonation of a 1000 sec. S. U. @ 100° F. naphthene base oil from which naphthenic acids had been previously removed.

Run C was for a duration of 240 hours in the four cylinder engine using an oil compounded with calcium sulphonate derived from the sulphonation of a 100 sec. S. U. @ 100° F. naphthene base oil from which naphthenic acids were not removed.

Run D was for a duration of 120 hours in the

single cylinder engine using an oil similar to that used in run A.

Run E was for a duration of 120 hours in the single cylinder engine using an oil similar to that used in run B.

Run F was for a duration of 120 hours in the single cylinder engine using an oil similar to that used in run C.

Table

Run	Total bearing corrosion, Mg loss	Appearance of engine
A	1,060	Clean.
B	191	Very clean.
C	1,510	Lacquer on piston skirts.
D	205	Clean.
E	70	Very clean.
F	291	Surfaces badly lacquered.

Accordingly the invention, in its broader aspects and in brief, comprises the following steps:

(*a*) Selection of a high boiling naphthene base oil for sulphonation;

(*b*) Removal of naphthenic acids and other acidic impurities from the selected oil;

(*c*) Sulphonation of the purified oil to yield oil soluble sulphonic acids;

(*d*) Removal of the sulphonic acids from the sulphonated oil and conversion of the same to polyvalent metal sulphonate while avoiding contamination by alkali metal salts; and

(*e*) Blending the polyvalent metal sulphonate into a suitable lubricating oil in suitable proportions.

It is obvious that steps (*d*) and (*e*) of the above tabulation may be combined into a single step by forming the polyvalent metal sulphonate directly in the oil, providing, of course, that the oil selected in step (*a*) is suitable for use in the finished oil.

The naphthene base oil selected for sulphonation should have at least about 90% of its constituents boiling above 375° F. at 2 mm. Hg absolute pressure. Under conventional methods of fractionally distilling lubricating oil stocks this would correspond to an oil having a viscosity above about 400 seconds S. U. at 100° F. However, an oil having a principal boiling range above 435° F. at 2 mm. Hg absolute pressure is preferred. Such a preferred oil would have a viscosity of 900 to 3000 seconds S. U. at 100° F.

The oil so selected is first freed from naphthenic acids and other acidic bodies, which may be accomplished by prolonged treatment with aqueous caustic alkali. Alternately, and preferably, the acidic bodies may be removed by distillation, under reduced partial pressure, in the presence of caustic soda, caustic potash, lime, or other alkaline material. Other methods of removing the acidic substances may suggest themselves. Although it has been found that the usual treatment with a selective solvent removes only a portion of the naphthenic acids, such treatment, either before or after the above caustic treatment, is desirable to remove the more reactive constituents of the oil which might otherwise form unstable sulphonation products.

The oil thus freed from the unstable impurities is treated with concentrated sulphuric acid, preferably between 98% H_2SO_4 and 15% free SO_3. The acid rate used for this treating step is from two pounds per barrel up to 100 pounds per barrel, depending upon the quantity of sulphonic acids desired in the treated oil. For an oil containing 1% of sulphonic acids, about 15 pounds of fuming sulphuric acid per barrel will be required and for oils containing higher percentages of sulphonic acids, higher rates of sulphuric acid per barrel are required. The temperature of the treatment may vary from below atmospheric up to about 200° F., a higher degree of sulphonation being obtained at the higher temperatures. Any method of agitation of the acid with the oil is suitable, although mechanical agitation in a closed system is preferred, particularly when elevated temperatures are employed. Agitation with air may be used, but is less desirable because of the tendency, more pronounced at elevated temperatures, to initiate oxidation reactions. The use of air may also involve the loss of appreciable quantities of SO_3. In order to obtain efficient mixing of high viscosity oils, the oil should be diluted with a low viscosity oil of great resistance to sulphonation. For this purpose a highly acid-treated light oil, such as kerosene or transformer oil, may be used, it being the purpose to reduce the viscosity without introducing any material which will produce sulphonic acids other than those desired. After treatment with the acid for a sufficient length of time, the acid sludge is completely separated from the oil. In order to separate the last traces of sludge, centrifuging or filtration may be required.

Following sulphonation the sulphonic acids contained in the oil may be removed from the oil, converted to the required polyvalent metal sulphonate and the latter added to the desired lubricating oil in the required proportion; or the sulphonic acids may be converted to the required metal sulphonate directly in the oil.

If it is desired to separate the acids, the separation and conversion to the metal sulphonate should, as stated above, be performed so as to avoid contamination by alkali metal sulphonate. The polyvalent metal sulphonate is then blended into an oil of suitable viscosity which may be of the paraffinic, naphthenic, or mixed-base type as may be required. From 0.1% to 5.0% of metal sulphonate has been found useful in supplying the desired properties to the oil, although best results are generally obtained with from 1% to 5%. Oils containing higher percentages of metal sulphonate may be manufactured and later blended with other suitable oil to meet the desired percentage. Such blending may be done by the manufacturer prior to sale or it may be done by jobbers or the ultimate consumer. In any event, such stock solutions, containing more than 5% of metal sulphonate are intended to come within the scope of the invention.

In the event that it is desired to convert the sulphonic acids to the polyvalent metal sulphonate directly in the oil, the sulphonated oil after complete removal of the acid sludge is contacted with an oxide, hydroxide, or water-soluble inorganic salt of the particular metal desired to be incorporated into the oil as an oil-soluble sulphonate. The preferred metal for this purpose is one of the alkaline earths, especially calcium. The metal salts or oxides can be added in dry form and subjected to intimate and prolonged agitation with the acid oil. Preferably a small amount of water is added which speeds up the reaction between the free sulphonic acids and the metal compound. For this purpose a quantity of water equal to about one or two percent of the volume of oil has been found satisfactory. Agitation is continued until the neutralization is complete, which point may, if desired, be determined readily by simple laboratory test. Follow-

ing neutralization the oil is completely dehydrated, for which purpose a flash distillation may be employed, after which the excess metal salt and other reaction products are removed by settling, followed by centrifuging or filtration, if necessary. Following conversion of the sulphonic acids to metal sulphonate the kerosene, transformer oil, or other diluent used is removed by distillation under reduced partial pressure.

When manufacturing the metal sulphonate directly in the oil attention should be given to certain features which are unimportant when the metal sulphonate is prepared separately and added to the lubricating oil.

First, the oil selected for sulphonation must also be chosen with regard to its suitability as the major constituent of the finished lubricating oil. The characteristics of naphthene base oils are well known in the art and proper selection for any given purpose is within the skill of the refiner. Ordinarily, oils which have been refined by the well known Edeleanu process, or other solvent refining process, are preferred by the trade, and such oils are well adapted for the present purposes. The sulphonation step and the presence of the metal sulphonate change the viscosity but little and any such change not anticipated may be adjusted by a final blending or reduction if desired.

Second, the degree of sulphonation should be carefully controlled so as to produce the required amount of sulphonic acids to produce the concentration of metal sulphonate desired in the finished oil. The required degree of sulphonation may be readily determined by simple laboratory tests for any given oil. It has been found expedient and, therefore, is a preferred embodiment of the invention, to deliberately carry the sulphonation beyond the desired concentration of sulphonic acids and, after conversion of the acids to metal sulphonate, to blend with the treated oil a sufficiently quantity of any suitable oil to produce the required concentration of sulphonate in the final blend. By proper choice of blending oil the viscosity and viscosity-index of the final blend can be controlled simultaneously with the concentration of sulphonate. As an example, a naphthenic base oil having a viscosity approximating S. A. E. 50 and a viscosity-index of about 30 may be sulphonated to yield as high as 10% of sulphonic acids dissolved in the oil, exclusive of the diluent used to reduce the viscosity as described above. At this point further sulphonation becomes very difficult. After conversion of the sulphonic acids to metal sulphonate and removal of the diluent, the oil may be blended with an S. A. E. 10 oil having a viscosity index of 100 (paraffin base oil) to give a finished oil containing 4% to 5% of metal sulphonate with an S. A. E. 30 viscosity and a viscosity-index of 70. The exact concentration of metal sulphonate in any such treated oil may be readily determined by an "ash" analysis.

In the foregoing description it has been shown that polyvalent metal sulphonates prepared from sulphonic acids derived from the sulphonation of specially selected and treated naphthene base oils have, when blended into lubricating oils, excellent ability to prevent oxidation and maintain engine cleanliness. It has also been pointed out that greater yields of sulphonic acids may be obtained from the sulphonation of naphthene base oils than from paraffin base oils. In accordance with a particular embodiment of the invention, it is contemplated to sulphonate blends of paraffin base and naphthene base oils; providing, of course, that the naphthene base oil in the blend is of high boiling range and has been freed from acidic impurities in accordance with the principles described above. Due to the higher yields of sulphonic acids obtainable from the naphthene base constituent of the blend, such a blend will yield the major portion of sulphonic acids from the naphthene base constituent even when the percentage of paraffin base oil in the blend is as high as 70%.

Hitherto it has not been deemed advisable to derive metal sulphonates from such blends due to the undesirable characteristics customarily exhibited by the metal sulphonates derived from the naphthene base constituents. By treating the naphthene base constituent of the blend in accordance with the principles outlined above, advantage can be taken of the greater yields obtainable over those obtainable when sulphonating straight paraffin base oils. This may be utilized to advantage when it is desired to prepare polyvalent metal sulphonate directly in the oil and the finished oil is required to have a viscosity index substantially greater than that of naphthenic oils. In such a case one may advantageously select a high boiling naphthene base oil, free the same from naphthenic acids and other acidic impurities, blend therewith the required amount of paraffin base oil to obtain the desired viscosity-index, sulphonate the blend, and convert the sulphonic acids to polyvalent metal sulphonate, as described above for naphthene base oil alone. By selection of a high viscosity naphthene base oil and a low viscosity paraffin base oil for such purpose the use of the diluent may be, in general, dispensed with as the viscosity of the blend will normally be sufficiently low to permit efficient mixing with the sulphonating agent. Following is an example of the preparation of a compounded lubricating oil in this manner:

220 gallons of a California lubricating distillate having a viscosity of 3000 seconds S. U. at 100° F. which had been Edeleanu treated were distilled under vacuum in the presence of 5 gallons of 40 Bé. caustic soda solution to remove naphthenic acids and to yield 215 gallons of purified oil. To the purified oil was added 285 gallons of Pennsylvania neutral having a viscosity of 200 seconds S. U. at 100° F. The resulting blend was agitated with 300 pounds of fuming sulphuric acid containing 15% free SO_3 for a period of one hour during which time the temperature rose from 85° F. to 110° F. The acid sludge was removed by settling following which the last traces of sludge were removed by centrifuging. The sulphonated oil was then agitated with 80 pounds of $Ca(OH)_2$ to which was added 10 gallons of water. The agitation was continued for three hours at a temperature of 80° F., following which the water was flashed off and excess lime was removed by filtration. This yielded a finished oil having the following properties:

Viscosity, sec. S. U. @ 100° F	537
Viscosity-index, Dean and Davis	79
Ash, percent as $CaSO_4$	0.35
Estimated calcium sulphonate, percent	3.5
Bearing corrosion after 120 hours in single cylinder Diesel engine, mg	73
Appearance of engine	Excellent

In the foregoing description the formation of oil soluble sulphonic acids from petroleum oils has been described as being accomplished by sulpho-

nation with concentrated sulphuric acid. By concentrated sulphuric acid, 66° Bé. acid up to fuming acid containing 50% free SO_3 is meant; although, as stated prior, a concentration between 98% H_2SO_4 and 15% free SO_3 is preferred. However, other sulphonating agents may be used. For example, chlorosulphonic acid, or sulphuric acid in conjunction with certain water absorbing ingredients, such as phorsphorous pentoxide, may be used to aid the sulphonation process.

As stated prior, the scope of the invention includes oils containing high percentages of sulphonate for use as stock solutions which are to be later blended with suitable oil to yield the required concentration of sulphonate. When it is desired to prepare such stock solutions and it is likewise desired to convert the sulphonic acids to the polyvalent metal sulphonate directly in the oil, the oil after neutralization with the metal oxide, hydroxide, or salt, may be subjected to a distillation with fire and steam, preferably under vacuum, for the purpose of concentrating the additive by distilling off part of the oil. In this manner the soap content of the residual oil can easily be brought to the desired concentration within a wide range. It is found that, by such concentration process, the stability of the sulphonate additive is further improved. Such concentration causes the breakdown of the less stable constituents of the sulphonate with a resulting precipitation of a small quantity of inorganic matter, which should preferably be filtered from the oil. If desired, such concentration may be conducted in the same operation as the dehydration step. Likewise, if a low boiling oil is used to reduce the viscosity during sulphonation as described previously, the subsequent removal of the same may be combined with the concentration, if desired.

The terms paraffin base oils and naphthene base oils are used herein in accordance with the customary practice of the petroleum industry to differentiate oils with respect to their dominant characteristics. Paraffin base is applied to oils typical of those derived from Pennsylvania crude oils. These are characterized by having a high viscosity index and relatively high boiling range for a given viscosity. On the other hand, naphthene base oils have low viscosity indices, relatively low boiling ranges for a given viscosity, and generally contain appreciable quantities of naphthenic acids, phenols, and the like. Typical examples of naphthene base oils, to which the invention is particularly adapted, are those derived from California crude oils, especially those produced in the San Joaquin Valley.

Oils are known which have properties intermediate between the true naphthene and paraffin types. These are generally referred to as "mixed-base" oils. For the purposes of this invention such "mixed-base" oils are to be considered the equivalent of naphthene base oils providing they contain appreciable quantity of naphthenic acids or similar organic acids. If naphthenic acids are absent, such oils may be used, if desired, instead of the paraffin base oils in the blends described herein.

Unless otherwise specified, the terms "high boiling" and "high molecular weight" applied herein to petroleum oils are intended to mean oils of sufficiently high molecular weight that the main constituents thereof boil above about 375° F. at 2 mm. Hg absolute pressure. Similarly, "low boiling" and "low molecular weight" oils mean oils boiling below such temperature at said pressure. As applied to sulphonic acids, or metal salts thereof, similar terms may be used according to the molecular weight, or boiling range, of the petroleum oil from which the sulphonic acids are derived.

In the claims the terms "polyvalent metal base" and "alkaline earth metal base" are used to denote an oxide, hydroxide, or salt of a polyvalent metal or alkaline earth metal respectively, suitable for converting sulphonic acids into the corresponding metal sulphonate.

We claim:

1. A method of preparing a lubricating oil having reduced tendency toward oxidation, ring-sticking, and corrosion which comprises: removing napthenic acids and other acidic substances from a naphthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, treating the purified oil with a sulphonating agent to provide sulphonic acids dissolved in the oil, removing the spent sulphonating agent, converting the sulphonic acids to polyvalent metal sulphonate free of alkali metal sulphonate and incorporating the same in a hydrocarbon lubricating oil in oxidation inhibiting amount.

2. A method according to claim 1 in which the principal constituents of the naphthene base oil have boiling points above 435° F. at 2 mm. Hg absolute pressure.

3. A method according to claim 1 in which the sulphonating agent is concentrated sulphuric acid.

4. A method according to claim 1 in which the sulphonating agent is sulphuric acid having a concentration between 98% H_2SO_4 and 15% free SO_3.

5. A method according to claim 1 in which the amount of polyvalent metal sulphonate in the finished oil is in excess of 1%.

6. A method according to claim 1 in which the polyvalent metal sulphonate is an alkaline earth sulphonate.

7. A method according to claim 1 in which the polyvalent metal sulphonate is calcium sulphonate.

8. A method according to claim 1 in which the naphthenic acids are removed from the naphthene base oil by distillation at reduced pressure in the presence of caustic soda.

9. A method of preparing a lubricating oil having reduced tendency toward oxidation, ring-sticking, and corrosion which comprises: removing naphthenic acids and other acidic substances from a naphthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, treating the purified oil with a sulphonating agent to provide sulphonic acids dissolved in the oil, removing the spent sulphonating agent, removing the sulphonic acids from the oil and converting said acids to polyvalent metal sulphonate while avoiding the formation of any alkali metal sulphonate, and adding the polyvalent metal sulphonate to a hydrocarbon lubricating oil in oxidation inhibiting amount.

10. A method of preparing a lubricating oil having reduced tendency toward oxidation, ring-sticking, and corrosion which comprises: removing naphthenic acids and other acidic substances from a naphthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, treating the purified oil with a sulphonating agent to provide sulphonic acids dissolved in the oil in amount greater than 0.1%, removing the spent sulphonating agent,

treating the oil containing sulphonic acids with a polyvalent metal base to convert the sulphonic acids to polyvalent metal sulphonate dissolved in the oil, and removing any unreacted polyvalent metal base.

11. A method of preparing a lubricating oil having reduced tendency toward oxidation, ring-sticking, and corrosion which comprises: removing naphthenic acids and other acidic substances from naphthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, treating the purified oil with a sulphonating agent to provide sulphonic acids dissolved in the oil in amount greater than 0.1%, removing the spent sulphonating agent, treating the oil containing sulphonic acids with an excess of lime in the presence of water to convert the sulphonic acids to calcium sulphonate dissolved in the oil, and removing the water and the unreacted lime.

12. A method according to claim 11 in which the sulphonation produces sulphonic acids dissolved in the oil in amount greater than 1.0%.

13. A method of preparing a lubricating oil having reduced tendency toward oxidation, ring-sticking, and corrosion which comprises: removing naphthenic acids and other acidic substances from a nahpthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, blending the purified oil with a paraffin base oil in amount not greater than 70% of the blend, treating the blend with a sulphonating agent to provide sulphonic acids dissolved in the blend, removing the spent sulphonating agent, removing the sulphonic acids from the blend and converting said acids to polyvalent metal sulphonate while avoiding the formation of any alkali metal sulphonate, and adding said polyvalent metal sulphonate to a hydrocarbon lubricating oil in oxidation inhibiting amount.

14. A method of preparing a lubricating oil having reduced tendency toward oxidation, ring-sticking, and corrosion which comprises: removing naphthenic acids and other acidic substances from a naphthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, blending the purified

oil with a paraffin base oil of lubricating oil viscosity in amount not greater than 70% of the blend, treating the blend with a sulphonating agent to provide sulphonic acids dissolved in the blend, removing the spent sulphonating agent, treating the blend containing sulphonic acids with a polyvalent metal base to convert the sulphonic acids to polyvalent metal sulphonate dissolved in the blend, and removing any unreacted polyvalent metal base.

15. A method of preparing a lubricatng oil having reduced tendency toward oxidation, ring-sticking, and corrosion which comprises: removing naphthenic acids and other acidic substances from a naphthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, blending the purified oil with a paraffin base oil of lubricating oil viscosity in amount not greater than 70% of the blend, treating the blend with a sulphonating agent to provide sulphonic acids dissolved in the blend, removing the spent sulphonating agent, treating the blend containing sulphonic acids with lime in the presence of water to convert the sulphonic acids to calcium sulphonate dissolved in the blend, and removing the water and unreacted lime.

16. A method of preparing a lubricating oil containing polyvalent metal salts of sulphonic acids derived from sulphonating a highly viscous naphthene base oil which comprises: removing naphthenic acids and other acidic substances from a highly viscous naphthene base oil whose principal constituents have boiling points above 375° F. at 2 mm. Hg absolute pressure, diluting the oil with a low viscosity oil having high resistance to sulphonation, treating the purified and diluted oil with a sulphonating agent to provide sulphonic acids dissolved in the oil, removing the spent sulphonating agent, treating the oil containing sulphonic acids with a polyvalent metal base to convert the sulphonic acids to polyvalent metal sulphonate dissolved in the oil, and then removing said low viscosity oil and any unreacted polyvalent metal base.

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