

June 2, 1964

W. B. WHITNEY ETAL

3,135,693

PROCESS FOR PREPARATION OF IMPROVED LUBRICATING COMPOSITIONS

Filed Sept. 10, 1962

2 Sheets-Sheet 1

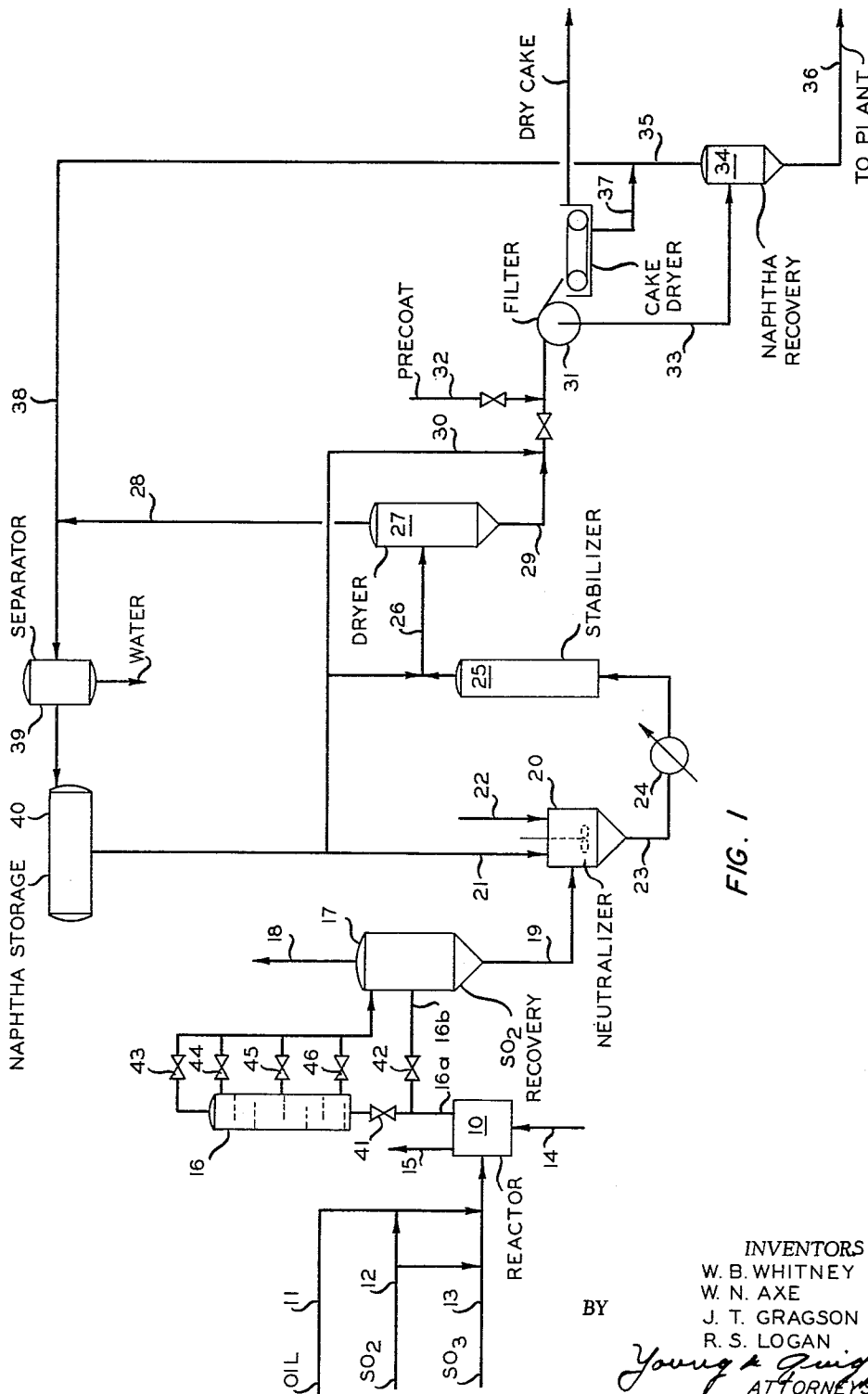


FIG. 1

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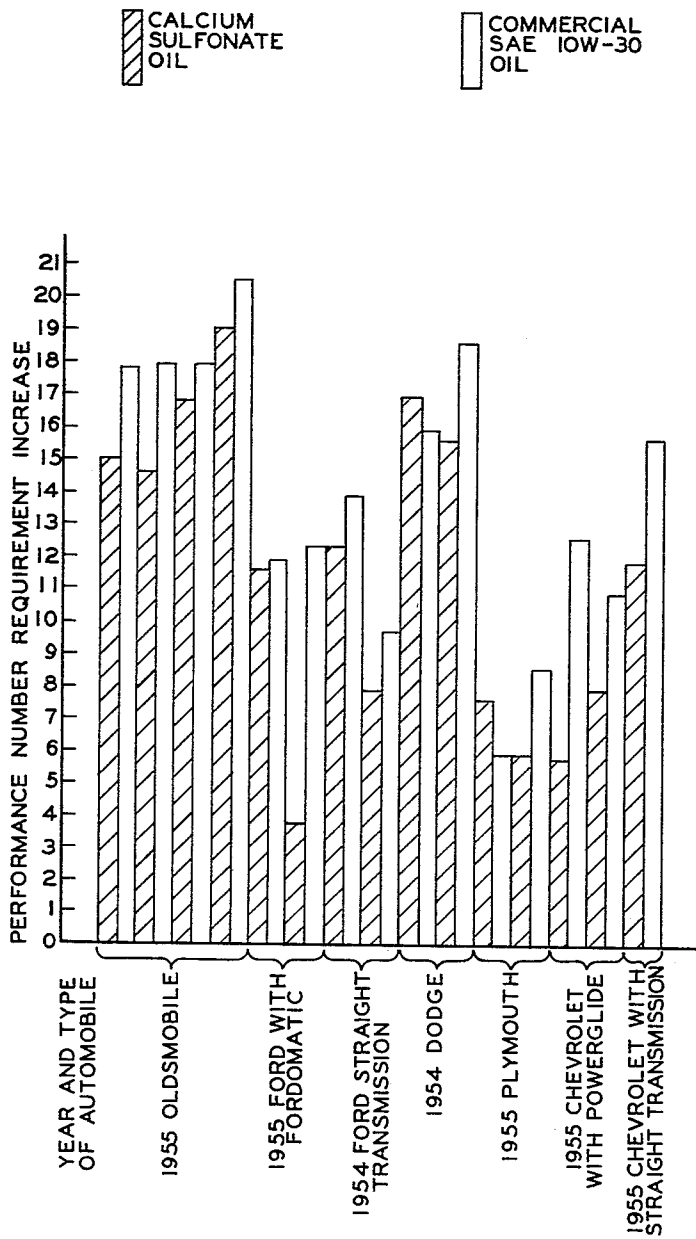


FIG. 2

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1

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PROCESS FOR PREPARATION OF IMPROVED LUBRICATING COMPOSITIONS

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19 Claims. (Cl. 252—33)

This invention relates to an improved petroleum sulfonation process from which novel metal petroleum sulfonates and substantially sulfonate-free oils are obtained as principal products. In one aspect this invention relates to the sulfonation of solvent-extracted, dewaxed, high viscosity hydrocarbon fractions. In another aspect it relates to petroleum lubricants prepared by adding to selected base stocks, novel metal petroleum sulfonates and/or the sulfonate-free oil resulting from the sulfonation process.

This is a continuation-in-part of our copending application Serial No. 665,985, filed June 17, 1957, now abandoned.

Copending application, Serial No. 478,839, filed December 30, 1954, by W. B. Whitney, now abandoned, described a method for preparing oil soluble metal petroleum sulfonates from highly refined, solvent extracted, high molecular weight petroleum stocks by treatment with a sulfonating agent, neutralization of the resulting oil-acid mixture with anhydrous ammonia, extraction of an ammonium petroleum sulfonate with an organic solvent, and conversion of the ammonium petroleum sulfonate to the metal petroleum sulfonate by reaction with an excess of a metal salt or hydroxide. It had heretofore been considered commercially impractical to produce oil-soluble sulfonates from high molecular weight hydrocarbon fractions such as a bright stock having a viscosity of about 200 SUS at 210° F. because of the virtual impossibility of separating an acid phase from the sulfonation mixture. Furthermore, complete neutralization of the total sulfonation mixture with an aqueous hydroxide, such as calcium hydroxide, results in intractable emulsions which are not amenable to conventional solvent extraction processes for metal sulfonate recovery.

Combustion chamber deposit formation in automotive engines has become a critical problem in recent years with the introduction of higher compression ratio engines. The generally higher initial octane number requirement of these new engines and the increase in octane number requirement after a few thousand miles of normal driving, which results in the formation of combustion chamber deposits, are creating a growing demand for gasoline of higher anti-knock quality. The petroleum industry has been searching for methods or means to eliminate or reduce combustion chamber deposit formation in order to minimize engine demand for higher anti-knock quality gasoline.

It would appear that an obvious solution to the problem of octane requirement increase would be to eliminate all high viscosity oils from the crankcase oil formulations; however, if this is done lubrication to valves and valve lifters becomes inefficient and may lead to malfunctioning of the engine. Furthermore, it has been demonstrated that all neutral oils can result in excessive wear of cylinder walls and consequently in loss of power.

2

In accordance with the present invention, an improved process is provided for making metal petroleum sulfonates from highly refined, high molecular weight petroleum stocks which results in a superior lube oil additive and furthermore we have discovered that the concomitant product oil provides a superior lube oil blending stock for preparing lubricating oil compositions in that the finished lube oil demonstrates remarkable resistance toward octane requirement increase.

It is an object of this invention to provide a process for preparing an improved metal petroleum sulfonate from high molecular weight petroleum stocks. It is also an object of this invention to provide simultaneously an improved metal petroleum sulfonate useful as a lubricating oil additive and a superior lubricating blending oil, with respect to octane requirement increase characteristics. It is a further object of this invention to provide an improved lubricating oil blending stock. It is still another object of this invention to provide improved lubricating oil compositions. Other and further objects of this invention will be apparent to one skilled in the art upon study of the disclosure of the present invention.

Broadly, the invention contemplates sulfonating a highly refined, high molecular weight petroleum fraction with liquid SO_2 dissolved in an inorganic solvent, neutralizing the reaction mixture with the carbonate, oxide or hydroxide of a metal, heat treating the neutralization reaction mixture to stabilize the sulfonate with respect to ferrous corrosion, expelling moisture, removing unreacted inorganic salts and solids, and recovering a mixture of metal sulfonate and product oil, i.e., SO_2 treated bright stock, as the products; or blending the resulting composition with additional product oil resulting from a sulfonation reaction as described above. The product oil resulting from such sulfonation process has superior lubricating oil qualities with respect to octane requirement increase values.

The sulfonation base stock, sulfonating agents, and metals suitable for preparing the metal petroleum sulfonates are substantially the same as those disclosed in the above-referred to copending application, Serial No. 478,839 except that the higher viscosity base stocks, liquid SO_2 in liquid SO_2 as sulfonating agent, and calcium as the metal, are preferred. Thus, the base stock is selected from the more viscous bright stock fractions of petroleum. A petroleum fraction having a viscosity of at least 90 SUS at 210° F. will produce a satisfactory petroleum sulfonate for many purposes. The deasphalted and solvent-refined petroleum fractions having a viscosity of about 140 to about 720 SUS at 210° F. are preferred because the product oil resulting from the sulfonation reaction possesses the characteristic of reducing octane requirement increase of crankcase oils when blended with commercial lube oil base stocks and the sulfonate of this invention. A specifically preferred sulfonation stock for low temperature dispersing properties as well as low octane requirement increase properties is a propane-fractionated, solvent-extracted and dewaxed Mid-Continent oil of about 200 to 230 SUS at 210° F. and having a viscosity index of about 90 to 100 or even higher. A Mid-Continent oil is more precisely defined as a mixed base or intermediate base oil in "The Science of Petroleum," volume 1, page 7, Oxford University Press, London, New York and Toronto, 1938.

The base of a crude petroleum is defined therein as follows:

"The 'base' of a crude petroleum is descriptive of the chemical nature of its main constituents. A petroleum may be described as paraffin base, asphalt base, or mixed base (intermediate base), according as paraffin wax, asphalt, or both paraffin wax and asphalt are present in the residue after distillation of the lighter components. Typical representatives of these three classes are Pennsylvanian, Mexican and Mid-Continent petroleum respectively."

The residual material discarded from the propane fractionation step contains the rejected asphalt and more aromatic oils. The lube oil fraction, recovered in a propane fractionation step after removal of the SAE-50 lube stock, is extracted with a selective solvent which will separate the paraffinic hydrocarbons from the more aromatic-type hydrocarbons for removal of these more aromatic type hydrocarbons to prepare the preferred feed stock. The raffinate from the solvent extraction step is then dewaxed.

Sulfonating agents which can be used in the sulfonation step of the process include liquid SO_3 in sulfuric acid, i.e., fuming sulfuric acid and liquid sulfur trioxide, e.g., liquid sulfur trioxide in liquid sulfur dioxide. We have found, however, that gaseous SO_3 is not satisfactory as a sulfonating agent because of low yield of sulfonate and production of side reaction products such as products of oxidation. We have found that liquid SO_3 alone or in a diluent or solvent such as ethylene chloride similarly is unsatisfactory.

All metals are suitable for preparing the petroleum sulfonates, however, the alkaline earth metals are preferred and calcium is especially preferred in the practice of this invention.

Sulfonation temperatures can be controlled within the range of about 50 to about 200° F. with the preferred operating range being between about 80 and about 150° F. At temperatures above about 200° F., excessive oxidation with liberation of sulfur dioxide takes place. A reaction time of 20 to 90 minutes is preferred when fuming sulfuric acid is utilized as the sulfonating agent in order to provide optimum yield and quality of products. When sulfur trioxide, e.g., sulfur trioxide in sulfur dioxide, is utilized as the sulfonation agent the reaction rate is greatly accelerated and the reaction has been found to be substantially completed in the time required to accomplish suitable contact of the oil with the sulfur trioxide. A device for effecting suitable contact of the oil and sulfonation agent with a minimum of heating of the reactants is disclosed and claimed in copending application Serial No. 116,583, filed June 12, 1961, by R. S. Logan.

With 20 percent fuming sulfuric acid as the sulfonating agent, the acid-oil ratio can be in the range from about 0.1:1 to about 0.7:1 or even 1:1 to produce the petroleum sulfonates of the invention. However, when it is desired to produce concomitantly with the metal sulfonate a product oil having the unique property of reducing octane requirement increase (ORI) characteristics in a finished oil, a higher minimum acid-oil ratio of 0.2:1 is required. The preferred range of acid-oil ratios for the simultaneous production of metal petroleum sulfonate and ORI-reducing product oil is in the range of about 0.3 to about 0.6. When an acid-oil ratio greater than about 1:1 is employed, the sulfonate produced is dark, almost black, and tarry in contrast to the red, resinous product obtained employing the preferred acid-oil ratios. When SO_3 in SO_2 is the sulfonation agent, SO_3 -oil weight ratios are maintained equivalent to those available from the 20 percent fuming sulfuric acid values cited hereinbefore. In other words, the SO_3 -oil ratio can be in the range of about 0.02 to 0.2 with the more preferred range being about 0.06 to 0.12. SO_3 -oil ratios can be controlled by varying the rate of flow of the oil or of the SO_3 -containing medium or both. The acid-oil ratios above are weight ratios.

The sulfonation reaction can be carried out at atmos-

pheric pressure although pressures greater or less than atmospheric also can be employed if desired. It is usually preferred to carry out the reaction at sufficient pressure to maintain SO_2 in liquid phase.

In order to produce a treated bright stock, i.e., product oil recovered from the sulfonation reaction, capable of appreciable ORI reduction, it is necessary to effect sulfonation of substantially all of the aromatic molecules present in the feed stock used. In order to obtain this necessary degree of conversion, oleum/oil weight ratios or SO_3 /oil weight ratios in the ranges hereinbefore set forth are required.

A distinguishing feature of this process over conventional sulfonation processes is the improvement in the case of separating solids such as metal hydroxides, sulfates and sulfites from the neutralized reaction mixture. Because of the outstanding dispersive properties of the high molecular weight sulfonates of this invention, ordinary centrifugation and filtration procedures are not commercially practicable. We have found that careful control of the neutralization, stabilization and dehydration steps will permit satisfactory precoat filtration rates. The neutralized and stabilized mixture, as hereinafter described, is diluted with about an equal volume of a hydrocarbon solvent such as Stoddard solvent to cool the total resulting mixture to about 240° F. This mixture is then flashed to atmospheric pressure and water is then removed by heating and steam stripping at a temperature below about 240° F. The moisture content of the feed to the filter will normally be less than about 0.5 weight percent, usually about 0.2 to 0.3 weight percent. Filtering can be accomplished successfully at a moisture content of less than about 1 weight percent.

The petroleum sulfonate plant balance product is added to the base oil in an amount sufficient to obtain the desired degree of improvement characteristics of the oil. The sulfonate plant balance product can be added in amounts of about 0.2 to about 30 weight percent of finished oil. The concentration of sulfonate alone is normally in the range of about 0.1 to about 15 weight percent of the finished oil and the preferred concentration of plant balance sulfonate product is in the range of about 3 to 20 weight percent of the finished oil. The preferred concentration of calcium petroleum sulfonate in the finished oil is in the range of about 1.5 to 10 weight percent.

In the process of the present invention the product oil (SO_3 treated bright stock) and alkaline earth sulfonate are produced in a weight ratio of about 1 to 1 and the product is referred to as "plant balance." In order to obtain maximum ORI reduction, an excess of product oil over and above the normal plant balance is ordinarily added. The reduction in ORI is more pronounced when product oil resulting from the sulfonation of the higher viscosity oils is used. Thus if a 200 SUS at 210° F. oil is sulfonated a marked reduction in ORI results when the product oil and the alkaline earth sulfonate are used in the ratio as produced. When a commercial solvent refined bright stock of 150 SUS at 210° F. oil is sulfonated a reduction in ORI of lesser magnitude results from using the product oil and the sulfonate in the ratio as produced. The product oil resulting from sulfonation of a 200 SUS at 210° F. oil has a viscosity of about 150 SUS at 210° F., and therefore, the viscosity of the finished oil will determine the upper limit of the amount of this oil which can be utilized. In general, it is preferred to use the product oil in the weight ratios of about 1 to 1, to about 2 to 1 with respect to the sulfonate used in the finished oil.

In a more specific application of the invention, the oil base stock is intimately contacted with the sulfonation agent. For example, the contacting can conveniently be accomplished by mixing the oil and acid streams in a centrifugal pump. When fuming sulfuric acid is the sulfonation agent the mixture is passed to a reaction chamber maintained at reaction temperature, through which the mixture passes with a minimum of mixing over a

period of time in the range of 20 to 90 minutes. When liquid sulfur trioxide in liquid sulfur dioxide is the sulfonating agent the reaction chamber can be partly or wholly bypassed. The effluent from the reaction chamber is neutralized by running it into an agitated vessel containing a slurry of alkaline earth hydroxide, e.g., calcium hydroxide, water and a hydrocarbon diluent such as Stoddard solvent or kerosene. The temperature of the contents of this neutralizing vessel is not critical with respect to neutralization, but is ordinarily held between about 160 to 200° F. for a period of time sufficient to neutralize the reaction mixture because the subsequent filtering step is greatly benefited by neutralizing at the above temperature.

In addition to neutralization of acid, an additional treatment above 360 and up to about 400° F. at the vapor pressure of the mixture, for a minimum time of about 10 minutes, is required to render the sulfonate completely noncorrosive to engine cylinder walls and piston rings. The sulfonate is noncorrosive when the vapors evolved from the oil phase being neutralized at 500° F. do not turn blue litmus paper red. This simple test is referred to as the acid vapor test. After this heat treatment, the slurry is diluted with a hydrocarbon diluent, cooled to about 240° F., is then flashed to atmospheric pressure and steam stripped at a temperature below about 240° F. to remove substantially all of the water. Other methods of dehydration can be used which will reduce the water content to a maximum of about 0.5 weight percent or less.

In preparing the sulfonates of the invention it has been found that an excess of calcium hydroxide, over the stoichiometric amount, is required in the neutralization and heat treatment steps. The minimum amount of aqueous lime slurry required for neutralization will be that which will enable the product to pass the acid vapor test. The minimum amount of aqueous lime slurry will depend upon the acidity of the sulfonate effluent, the alkalinity and particle size of the lime, the neutralizing and treating temperatures, and other process variables. The minimum amount of lime can easily be determined by the acid vapor test.

The maximum amount of aqueous lime slurry will depend upon the solvent utilized to dilute the feed to the filtration step following heat treatment and dehydration of the neutralized reactor effluent. When a ketone such as methyl isobutyl ketone is utilized as the diluent, or as an appreciable portion of the diluent, it has been found necessary to limit the maximum amount of aqueous lime slurry to about 1.25 times the minimum required for the product to pass the acid vapor test in order to produce a sulfonate having the superior properties of the sulfonate of the invention. The ash content of the plant balance ratio of sulfonate and product oil should not be more than about 6 weight percent as CaSO_4 in order to obtain a product exhibiting the most favorable characteristics as a lube oil additive. Similarly the base number of the plant balance product should be more than 7 and will usually be between about 7.5 and 8.5 and will seldom be above about 12. When a ketone is utilized as diluent in the filtering step and more than about 1.25 times the required minimum of aqueous lime slurry is utilized in the neutralization step, the ash content is increased without a corresponding increase in the base number and the product is adversely affected.

If no ketone is utilized in the filtering step, an excess of lime water slurry of great magnitude does not adversely affect the product because neither the ash content nor the base number is appreciably affected by such excess. If a light hydrocarbon solvent such as naphtha including Stoddard solvent, normal heptane and the like is used to dilute the dehydrated product for filtering the base number of the product will be more than 7, and the ash content, as calcium sulfate, will be about 4.5 to 5.5 weight percent. An excess of not more than about 1.25 times the minimum amount of aqueous lime water slurry re-

quired for the product to pass the acid vapor test will usually be utilized for reasons of economy. Treating the neutralized product at about 360–370° or higher for a period of about 10 minutes will produce satisfactory base number in the product if sufficient lime is present. A temperature substantially below about 360–370° F. is not sufficient because the base number of the product remains at an unsatisfactorily low level even though additional lime is added in the treating step. The treatment of the neutralized product at a temperature of about 360–370° F. or higher should be continued for at least 10 minutes. Additional treating time produces no deleterious effect on the product but, similarly, provides no measurable advantage.

The dehydrated mixture is then filtered and the filtration step is facilitated by diluting the mixture with several volumes of light hydrocarbon, such as Stoddard solvent and is also facilitated by the addition of a filter aid. The solvent is then removed from the filtrate by a flashing step similar to that used in neutralization and dehydration and the product comprising the metal petroleum sulfonate and the product oil is recovered.

The metal petroleum sulfonates are separated from the accompanying oil by means of extraction with propane and/or butanes under appropriate conditions of temperature and pressure. Partial separation of oil and sulfonate can be accomplished by extraction with conventional polar solvents or by distillation but in all cases where such procedures are applied to the oil-sulfonate solution of this invention, substantial quantities of sulfonate remain in the oil and similar quantities of oil remain in the sulfonate. The light hydrocarbons, propane, isobutane, and normal butane, have been found to have a unique and unexpected selectivity for this separation, producing under appropriate conditions, substantially ash-free oil and oil-free sulfonates. Using propane as the solvent, extraction temperatures of 150 to 200° F. are required at pressures of about 640 p.s.i.g. Lower temperatures result in excessive inclusion of sulfonate in the extract. With normal butane, lower pressures of about 400 to 500 p.s.i.g. are adequate, but to achieve selectivity, the temperature range must be held between 290 and 305° F. The conditions required when isobutane is required are intermediate those for propane and for normal butane.

The nature of the residual oil (product oil) is determined primarily by the feed stock hydrocarbon oil and sulfonation reaction conditions. It follows then that recovery of this oil from a different sequence of process conditions subsequent to the sulfonation step will have little or no influence on the efficacy of the product oil in influencing octane-requirement-increase. Thus, the product oil can be used which results from sulfonating the feed stock with SO_3 in SO_2 or with 20 percent oleum, neutralizing the reaction mixture with ammonia, extracting the ammonium petroleum sulfonates with an organic solvent and converting the ammonium sulfonate to a metal sulfonate. However, this generalization is only true when propane or a butane is used to separate the SO_3 refined oil from the sulfonate. This critical limitation stems from the fact that conventional sulfonate solvents such as alcohols, ketones and the like are incapable of producing sulfonate-free oil and oil-free sulfonates. Hence, the use of a solvent, subsequent to the sulfonation step, which will change the composition of either the sulfonate or the product oil by selective solvent action can result in compositions markedly different from those of the invention.

The products of this invention can be incorporated into finished lubricating oil compositions in several combinations depending upon specific service requirements. For example, in the case of heavy duty oils, such as those used in trucks, busses, and general diesel applications, the oil-free sulfonate is blended with suitable base stocks. In all general duty crankcase oil where ORI is not critical, the unfractionated combination of sulfonate and product

oil is blended with appropriate base oils. In the case of high compression ratio engines, e.g., ratios of 8:1 to 10:1 or higher, there is added to the base oils, sufficient oil-free metal petroleum sulfonate to provide adequate detergency, and product oil substantially in excess of that normally present in the unfractionated total product of the sulfonation process. In variations of blending, the metal sulfonate components will provide high quality oils as required in Ordinance qualification tests, and outstanding performance with respect to sludge formation in stop-and-go engine operation. Reduction in octane requirement increase is primarily a function of the quantity of sulfonate-free product oil included along with the metal sulfonate.

The product oil resulting from the sulfonation of a refined bright stock in the viscosity range 190–210 SUS at 210° F. according to the process of the invention, as hereinbefore described, is a dark, red-colored oil by transmitted light and has a viscosity of about 145 to about 155 SUS at 210° F. The ASTM color is 6+. The molecular weight is above 600, the viscosity index is above 100. The aromatic rings per molecule are about 0.5 or less (see Table V) and the sulfated ash content is less than 0.2 weight percent.

The metal petroleum sulfonates of the invention are dark red, resinous products having a molecular weight (average) of about 2000 to about 4000. These sulfonates are insoluble in water and are soluble in lube oils.

FIGURE 1 of the drawing is a schematic flow diagram of a plant for producing the petroleum sulfonate of the invention; and

FIGURE 2 of the drawing is a bar graph showing results of field tests wherein the sulfonate of the invention was utilized.

In FIGURE 1, a petroleum hydrocarbon fraction as hereinbefore described is introduced to reactor 10 via conduit 11 and sulfur trioxide is introduced to reactor 10 via conduit 13. Each stream is diluted with sulfur dioxide and the two diluted streams are mixed as they enter the reactor 10. When fuming sulfuric acid is utilized as the sulfonating agent, the sulfur dioxide is usually omitted and the hydrocarbon fraction is diluted, if desired, with a low boiling liquid hydrocarbon. Cooling water is introduced to the indirect heat exchange jacket of reactor 10 via conduit 14 and is removed therefrom via conduit 15 so as to maintain the reaction temperature at about 110 to 130° F. The effluent from reactor 10 is passed to time tank 16 for completion of the reaction, in case fuming sulfuric acid is utilized as the sulfonating agent, and thence to flash tank 17 where sulfur dioxide is vaporized and removed via conduit 18 for reuse. When the sulfonating agent is sulfur trioxide, the time tank 16 can be completely bypassed by closing valve 41 in line 16a and opening valve 42 in line 16b; or intermediate portions of time tank 16 can be employed by leaving valve 42 closed and valve 41 open and closing valve 43 and opening any one of valves 44, 45 or 46. The substantially sulfur dioxide-free reaction product removed from flash tank 17 is then passed via conduit 19 to neutralizer 20 wherein the reaction product is admixed with naphtha introduced via conduit 21 and an aqueous slurry of lime (calcium hydroxide) introduced via conduit 22. The slurry of reaction product, naphtha, lime and water, removed from neutralizer 20 is passed via conduit 23 and heater 24 to stabilizer 25, maintained at a temperature of about 360–370° F. for completion of the neutralization reaction. The neutralized slurry is passed via conduit 26 to dryer tower 27 where water, as an azeotrope with naphtha, is removed overhead via conduit 28. The dryer tower bottoms are removed via conduit 29, diluted with naphtha via conduit 30 and passed to precoat filter 31 for removal of lime and other inorganic solids such as calcium sulfate. The filter 31 is precoat with filter aid introduced via conduit 32 periodically as is conventional with precoat filters. The dried plant balance calcium petroleum sulfonate, diluted with naphtha, is removed from the filter

via conduit 33 and passed to stripper 34. Naphtha is removed from stripper 34 via conduit 35. Petroleum sulfonate, plant balance, as finished product is removed from naphtha stripper 34 via conduit 36. Naphtha is recovered from drying the filter cake and is passed via conduit 37 to conduit 38. Naphtha in conduits 28, 35 and 37 is passed via conduit 38 to separator 39, where water is removed, and then to naphtha storage 40.

The following examples are specific embodiments of the invention which will be useful in illustrating the invention but are not to be construed as limiting the invention.

EXAMPLE I

Calcium Petroleum Sulfonate Preparation

A calcium petroleum sulfonate was prepared from a solvent refined, dewaxed lubricating oil fraction derived from Mid-Continent petroleum and having the following properties: Viscosity of 4278 SUS at 100° F., viscosity of 203 SUS at 210° F., and a viscosity index of 93. The charge stock identified as finished 250 stock was sulfonated with 20 percent oleum in a continuous operation. The acid to oil weight ratio was 0.4 and the temperature of the reaction was controlled at 140° F. The total reaction time was 70 minutes, including the mixing and soaking period. The system pressure was maintained at 16 p.s.i.g. Effluent from the sulfonation unit was run into a vessel of calcium hydroxide-water-Stoddard solvent slurry for neutralization and the mixture was agitated during the neutralization period. For each 100 pounds of oil charged to sulfonation, a slurry of the following composition was used for the neutralization: 36.5 pounds of calcium hydroxide, 110 pounds of water, and 50 pounds of Stoddard solvent. The neutralized mixture was then pumped through a 315° F. zone at 400 p.s.i.g., where its residence time was maintained at about 12 minutes. It was then heated to 450° F., flashed to atmospheric pressure and stripped to remove all of the water and most of the solvent. This material was mixed with the two volumes of Stoddard solvent, a diatomaceous earth filter aid was added, and the mixture was filtered to remove the solids. Solvent was removed from the filtrate by flash and stripping operations and the solvent free product was charged to a propane extraction unit. The following operating conditions were used in the propane extraction steps: solvent to oil ratio=6.5 by volume, pressure=650 p.s.i.g., and the temperature=170° F. The extraction operation yield was 46.2 weight percent sulfonate-free, product oil as the extract and 53.8 weight percent of calcium petroleum sulfonate as the raffinate.

Sulfated ash analyses of streams at various points in the process are shown in the following table on a solids- and solvent-free basis.

TABLE I

	Wt. percent
Feed to propane extraction unit	5.20
Propane soluble oil (product oil)	0.08
Propane bottoms (sulfonate)	9.7 to 10.2

A blend of 53.7 parts by weight of sulfonate and 46.3 parts by weight of Mid-Continent finished SAE-10 base stock was prepared to facilitate handling. This blend had an ash content of 5.41 weight percent and is designated as A100. The product oil was designated as A200 and the calcium sulfonate was designated as A300.

Octane Requirement Increase Test Procedure

The engine used in the octane requirement increase test procedure was a 1954 Oldsmobile with a standard compression ratio of 8.25:1 equipped with a standard two barrel carburetor. A 350 pound inertia wheel was connected directly to the engine through a flexible coupling, in order to simulate automobile coast-down and to create a high manifold vacuum during the closed throttle decelerations. An automatic engine and dynamom-

eter cyler was employed to control the test conditions during the period of deposit build-up. The engine was operated on a city-suburban cycle for approximately 150 test hours. The automatic repeating cycle consisted of 4 accelerations, 4 closed throttle decelerations, 4 different idle periods, 3 different 25 m.p.h. road load conditions, and 1 40 m.p.h. road load condition. Engine water-out and oil temperatures were controlled at $180\pm5^{\circ}$ F. and dynamometer loads were held to specified conditions ±0.5 B.H.P. The test schedule was maintained until combustion chamber deposit equilibrium was obtained. This normally required about 150 test hours. The final requirement was then determined, and the combustion chamber deposits were removed. This was followed by a clean check-back requirement. The difference between the final and clean check-back requirements is the requirement increase. The requirement increase can be expressed in terms of octane numbers or performance numbers. Performance number requirement increase (PNRI) was used to express the results in the examples because it is believed that this system is technically more correct than octane requirement increase (ORI). A table for converting octane numbers to performance number is shown in "ASTM Manual of Engine Test Methods for Rating Fuels," 1950 appendix, page 8.

Results obtained during the performance requirement increase tests are shown in the following examples.

EXAMPLE II

The general status of the ORI, or PNRI problem is illustrated by the data shown in the following table comparing two grades of commercial lube oils with a non-deposit-contributing synthetic oil. The synthetic oil was a polyoxyalkylene glycol motor oil which can be obtained from the Carbide and Carbon Chemicals Company.

TABLE II.—PERFORMANCE NUMBER REQUIREMENT INCREASE OF TYPICAL MOTOR OILS AS DETERMINATED IN A 1954 OLDSMOBILE ENGINE

Oil Grade	PNRI
Heavy duty 10W-----	17.4
Supplement I, 10W-30-----	10.1
Synthetic oil-----	4.6

EXAMPLE III

Influence of Product Oil on PNRI at Substantially Constant Sulfonate Concentration

TABLE III

[Lube Oil Formulation (SAE 10W-30 Supplement 1 Blend)]

Base oil, wt. percent	(A200) Product oil, wt. percent	(A300) Calcium sulfonate, wt. percent	PNRI
87.3	-----	7.5	9.6
82.3	6.2	6.2	8.2
72.5	14.1	8.2	5.1
72.4	13.5	7.3	3.5

NOTE.—The base oil in each blend was a refined paraffin base oil having viscosity characteristics necessary to provide a blend meeting SAE 10W-30 requirements. Each formulation contained about 4 weight percent of commercial viscosity index improver and about 1 weight percent of commercial bearing corrosion inhibitor.

A commercial grade SAE 10W-30 lube oil exhibited a PNRI value of 10.1 in a similar test, see Table II.

The data shown in Table III illustrate the reduction in PNRI obtained with increasing amounts of product oil and with a substantially constant amount of metal petroleum sulfonate. Any quantity of the special product oil of this invention used in combination with the calcium sulfonate of this invention results in an oil superior to the commercial control oil in PNRI performance.

EXAMPLE IV

TABLE IV.—PRODUCT OIL ENGINE PERFORMANCE AS A FUNCTION OF SULFONATION FEED STOCK
[Lube Oil Formulation (SAE 10W-30 Supplement 1 Blend)]

SAE 10 base stock, wt. percent	Calcium sulfonate, wt. percent	Product oil, wt. percent	Charge to sulfonation step	PNRI
67.0	7.5	20.3	105 SUS at 210 from 1st stage propane fractionation of Mid-Continent vacuum reduced crude.	9.2
72.5	8.1	14.1	206 SUS at 210 from 2nd stage propane fractionation of Mid-Continent vacuum reduced crude.	5.1
70.0	7.5	17.3	Mid-Continent solvent refined 150 SUS at 210 bright stock.	7.5

NOTE.—A blend similar to the first blend in Table IV wherein 105 SUS at 210 bright stock, which had not been subjected to sulfonation, was used (17.6 wt. percent) and a PNRI value of 9.6 was obtained, thus showing that the oil resulting from sulfonation of this fraction contributed very little to PNRI reduction. All bright stocks were solvent refined and dewaxed prior to the oleum treatment (sulfonation) and the sulfonate used in preparing the blends to SAE 10W-30 Supplement 1 requirements was derived from sulfonating a 250 stock. All formulations contained about 4 weight percent commercial viscosity index improver and about 1 weight percent commercial bearing corrosion inhibitor.

The results of the runs of Table IV show that the product oil resulting from sulfonating higher viscosity oil fractions imparts increasing reduction to PNRI. The product oil resulting from sulfonating a 105 SUS @ 210 viscosity oil contributed very little to PNRI reduction, whereas the oil resulting from sulfonating a 206 SUS @ 210 viscosity oil exhibited superior results. The product oil resulting from sulfonating a 150 SUS @ 210 viscosity oil provided PNRI reduction intermediate the other two.

EXAMPLE V

A solvent-refined and dewaxed oil fraction as described in Example I was treated at the rate of 0.1 pound of 20% oleum per 1 pound of oil instead of 0.4 pound of oleum per pound of oil, under process conditions substantially the same as in Example I. The product oil (SO₃ treated bright stock) constituted about 75 weight percent of the product instead of about 50 weight percent as in Example I. Inspection of the physical characteristics of the product oils resulting from the two different acid-oil ratios is not informative with respect to their ability to modify engine deposits. These product oils were used in substantially equal amounts in preparing SAE 10W-30 lube oils according to "Note" in Table III and were engine tested. The physical characteristics of the product oils and PNRI values of lube oils compounded from the product oils are shown in the following table.

TABLE V.—PHYSICAL CHARACTERISTICS OF PRODUCT OILS

Test	Acid/oil ratio of sulfonation	
	0.1/1	0.4/1
Viscosity, SUS at 100° F.-----	1,573	2,072
Viscosity, SUS at 210° F.-----	169.5	143.3
Viscosity Index-----	105	103
Aromatic rings/mol l.-----	0.5	0.3

¹ Aromatics determined by the n-d-M method described in "Aspects of the Constitution of Mineral Oils" by Van Nes and Van Westen, Elsevier Publishing Co., New York (1951) page 318.

TABLE V—Continued

INFLUENCE OF ACID/OIL SULFONATION RATIO ON PRODUCT OIL IN 10W-30 LUBE OIL		
Product oil/sulfonate weight ratios	Acid/oil sulfonation ratio	PNRI
1.5 to 1.....	0.1 to 1.....	11.1
1.7 to 1.....	0.4 to 1.....	5.1

The results of Example V as shown in the data in Table V show that severe sulfonation treatment is required to produce a product oil having the desired properties, with respect to the ability of the finished oil to modify engine deposits. The acid to oil ratio must be greater than 0.1:1 and is preferably in the range of 0.3:1 to 0.6:1.

It would appear that removal of aromatic constituents from the oil imparts the ability to modify engine deposits, i.e., reduce PNRI; however, tests have shown that removing aromatics, by silica gel chromatography, from a 250 stock, as identified in Example I, provided very little improvement over the untreated bright stock with respect to modifying engine deposits. Tests have indicated that the fraction of product oil adsorbed by silica gel is quite effective in controlling engine deposits in quantities as small as 1 percent or less; however, it will usually be more economical to utilize the total oleum-treated, sulfonate-free heavy bright stock.

EXAMPLE VI

Field tests were conducted using 15 automobiles of various makes and models. The tests were started with clean engines (deposits removed, etc.) and each automobile was operated for about 6 months with the oil being tested after which the engine was cleaned and the clean check-back value was determined. This procedure was followed with each oil tested. About one-half of the automobiles were filled with commercial oil and the others with the oil of Table VI at the beginning of the test so that an average of year round conditions was obtained. The automobiles were used in normal service.

A commercial SAE 10W-30, Supplement I lubricating oil was compared with a lubricating oil having the following composition:

TABLE VI.—COMPOSITION OF FIELD TEST OIL

Component:	
Base oil (SAE 10 base oil) ..weight percent..	72.5
Product oil (A200) ..do.....	6.0
Product oil and calcium sulfonate 1/1 ratio (plant balance) ..weight percent..	16.3
Commercial V.I. improver ..do.....	4.1
Commercial bearing corrosion inhibitor weight percent..	1.0
Commercial viscosity stabilizer ..do.....	0.1
Commercial foam depressant ..p.p.m..	500

Lube oil additives such as V.I. (viscosity index) improvers, corrosion inhibitors, foam depressants, and viscosity stabilizers are normally used in commercial SAE 10W-30 lube oil in substantially the same amounts as those shown in Table VI.

The results of the field tests are shown in Table VII and are graphically illustrated in FIGURE 2 of the drawing.

TABLE VII

Year and type of automobile	PNRI	
	Calcium sulfonate oil (Table VI)	Commercial SAE 10W-30 oil
1955 Oldsmobile (1).....	14.9	17.7
1955 Oldsmobile (2).....	14.5	17.8
1955 Oldsmobile (3).....	16.7	17.8
1955 Oldsmobile (4).....	18.9	20.4
1955 Ford, Fordomatic (1).....	11.5	11.8
1955 Ford, Fordomatic (2).....	3.7	12.2
1954 Ford, Straight Transmission (1).....	12.2	13.8
1954 Ford, Straight Transmission (2).....	7.8	9.6
1954 Dodge (1).....	16.8	15.8
1954 Dodge (2).....	15.5	18.5
1955 Plymouth (1).....	7.6	5.9
1955 Plymouth (2).....	5.9	8.5
1955 Chevrolet, Powerglide (1).....	5.8	12.5
1955 Chevrolet, Powerglide (2).....	7.9	10.3
1955 Chevrolet, Straight Transmission.....	11.8	15.6

The results of the field tests show that the lube oil of the invention is superior to the best grade of commercial oil presently available. The cause or causes for the trend reversals in runs (1) of the Dodge and Plymouth have not been determined.

In the following examples the lube oil of the invention was compared to a commercial 10W-30 oil in standard engine tests.

EXAMPLE VII

Chevrolet Cold Engine Sludge Test Procedure

TABLE VIII.—ENGINE-1953 CHEVROLET 6-CYLINDER VALVE-IN-HEAD, OPERATING CONDITIONS

Test, hours	Speed, r.p.m.	Load, b.h.p.	Temperature F.		Air-fuel Ratio	Spark advance, degrees before top dead center
			Water out	Oil		
2.....	500	0	125±2	-----	8.8 to 9.2	5
2.....	2,500	45	95±2	165±2	14.5±.5	38±3
2.....	2,500	45	200±2	245±2	14.5±.5	38±3

Test schedule—12 operating cycles of 6 hours as above.

Chevrolet Cold Engine Sludge Test

An SAE 10W-30 lube oil was blended having the following composition:

TABLE IX

	Volume percent
SAE-10 base oil	72.3
A200 (product oil)	15.5
A100 (calcium sulfonate, oil-free basis)	7.3
Commercial V.I. improver	4.0
Commercial bearing corrosion inhibitor	0.72
Commercial viscosity stabilizer	0.10

TABLE X.—CHEVROLET COLD ENGINE SLUDGE TEST RESULTS

Ratings	Oil of Table IX	Commercial 10W-30 lube oil	Perfect rating
Oil ring plugging.....	9.5	8.6	10.0
Piston varnish.....	7.5	4.1	10.0
Oil screen.....	9.8	9.0	10.0
Sludge rating.....	7.6	4.8	10.0
Over-all rating.....	84	63	100.0

EXAMPLE VIII

Caterpillar Diesel L-1 Test Procedure

This procedure involves operation of a special 1-cylinder diesel test engine for a total of 480 hours at a fixed speed and B.t.u. input, with the test oil as a lubricant. The test procedure is described in "CRC Handbook 1946" published by the Coordination Research Council,

13

Inc., at pages 2, 4, 7, et seq. The fuel used was that meeting military specification MIL-L-2104A, Supplement I and contained 1.0 weight percent sulfur.

Caterpillar Diesel L-1 Tests

An SAE 10W-30 grade motor oil was compounded having a composition of Table XI.

TABLE XI

Blend composition:	Volume percent
SAE 10 base oil	70.0
SAE 50 base oil	14.0
A100 (calcium sulfonate, oil-free basis)	5.8
A200 (product oil)	5.3
V.I. improver	4.1
Commercial bearing corrosion inhibitor	0.72
Commercial viscosity stabilizer	0.10

The lube oil of Table XI was subjected to the Caterpillar L-1 Diesel Engine Test along with several competitive SAE 10W-30 motor oils available on the market which were considered representative of the best available lube oils at the time of testing. The results of the tests are shown in the following Table XII:

TABLE XII.—120-HOUR DIESEL L-1 TEST RESULTS
[Perfect rating=100]

Oil tested	Top groove carbon rating	Lacquer rating	Over-all rating
Oil of Table XI	99	99.8	¹ 99.6
Commercial oil A	95	100	¹ 98.3
Commercial oil B	41	99.8	79.8
Commercial oil C	80	99.1	92.9
Commercial oil D	90	85.8	89
Commercial oil E	96	100	¹ 98.7
Commercial oil F	89	99.1	² 95.9

¹ Data indicate a 480 hour pass.

² Data indicate a border-line 480 hour pass.

The above data demonstrate the superiority of the sulfonate of the invention over the best lube oils available.

The results of the octane requirement increase tests show that a lube oil containing the petroleum sulfonate of this invention together with the product oil resulting from the sulfonation process exhibits a remarkable decrease in the octane requirement increase as compared to other lube oils and particularly when compared to a typical commercial premium grade all-weather lube oil.

The data of Examples VII and VIII illustrate the superior qualities of a lube oil prepared according to the process of this invention with respect to sludge formation as shown by the Chevrolet cold engine sludge tests and in performance as determined by the diesel L-1 tests.

EXAMPLE IX

A solvent-refined and dewaxed oil fraction as described in Example I was continuously sulfonated under process conditions substantially the same as in Example I, as follows:

Acid to oil, weight ratios	0.4
Reaction temperature, ° F.	130-140
Reaction pressure, p.s.i.g.	30
Reaction time, min.	70-80
Acid feed rate, lbs./hr.	8
Oil feed rate, lbs./hr.	20

The effluent from the sulfonation step was continuously neutralized by admixing same with a stream of lime (92 weight percent alkalinity as Ca(OH)₂) slurry made up as follows:

	Wt. percent
Water	57
Lime	20
Stoddard solvent	23

14

The "neutralized" stream was continuously heat treated and dehydrated as in Example I. The amount of lime was varied in a number of runs by varying the rate of slurry addition to the neutralization step and the products of the runs were diluted with mixtures of methyl isobutyl ketone and Stoddard solvent containing from 12.5 to 50 weight percent methyl isobutyl ketone, and filtered. The results of these runs are summarized in the following Table XIII.

TABLE XIII.—RELATIONSHIP OF AMOUNT OF ALKALINE EARTH HYDROXIDE TO ASH CONTENT OF SULFONATE PLUS PRODUCT OIL (PLANT BALANCE).

Run number	Sulfonator effluent, lbs./hr.	Lime slurry, lbs./hr.	Lime content of slurry, lbs./hr.	Sulfated ash content of plant balance product, wt. percent
1	28	47	9.4	(¹)
2 (average of 7 runs)	28	50	10.0	5.8
3 (average of 16 runs)	28	60	12.0	8.1
4 (average of 9 runs)	28	71	14.2	8.9

¹ Product not neutral. Vapors at 500° F. turned blue litmus paper red.

Lube oils were made to SAE 10W-30 specification according to "note" in Table III, using plant balance of sulfonate and product oil. The prepared lube oils were engine-tested, as hereinbefore described and the results are shown in Table XIV wherein sulfonate and product oil used corresponds to those of like run numbers in Table XIII.

TABLE XIV.—EFFECT OF AMOUNT OF ALKALINE EARTH COMPOUND IN NEUTRALIZATION AND TREATING STEPS ON PNRI OF FINISHED LUBE OIL.

Run No.	Ash in plant balance product, wt. percent	PNRI
1	Not tested	
2	5.0	6.1
3	8.0	10.3
4	Not tested	

The amount of ash in the plant balance ratio of sulfonate and product oil should not be more than about 6 weight percent in order to obtain a product exhibiting the most favorable characteristics as a lube oil additive. This is shown in the following Example X.

EXAMPLE X

Lube oils were made to SAE 10W-30 specification according to "note" in Table III using plant balance of sulfonate and product oil containing varying amounts of ash. The prepared lube oils were engine-tested and the results of Caterpillar diesel L-1 tests are shown in the following Table XV.

TABLE XV

Test No.	1	2	3	4
Number of test hours	120	480	120	240
Weight percent additive	11.3	11.3	11.0	11.0
Weight percent ash	6.7	6.7	8.0	8.0
Top groove carbon	94	86	92	74
Lacquer	99.2	96.5	99.2	99.4
Over-all rating	97.5	93.5	97.0	91.0
Indication of test	Border-line	Border-line	Fail	Fail
			Border-line	Pass

¹ 6.81% of 5.4% ash and 6.17% of 6.7% ash.

These data demonstrate that ash content of the plant balance product should be not more than about 6 weight

percent when a ketone is added prior to the filtration step.

EXAMPLE XI

A 100-gram sample of the 250 oil as described in Example I was sulfonated with 40 grams of oleum and allowed to react at 130° F. for 1¼ hours. The mixture was then diluted with 200 ml. of Stoddard solvent. To one centrifuge tube was added 50 ml. of the above mixture along with 5 ml. of water, shaken together. The mixture was centrifuged for 1 hour and examined. Three ml. of water was separated out as a separate lower phase. The oil layer was decanted and shaken in a centrifuge tube with 5 ml. of water and centrifuged for 1 hour. A green-colored emulsion resulted.

To another centrifuge tube was added 50 ml. of the mixture of reaction product and Stoddard solvent together with 10 ml. of water which were shaken together and centrifuged for 1 hour. Five ml. of water was separated as a lower layer.

A 50 ml. sample of the reaction product and Stoddard solvent was centrifuged for 1 hour. No visible separation occurred. Two ml. of water was added, and the sample shaken and centrifuged for 1 hour. About 1.8 ml. of water separated as a lower layer.

A 50 ml. sample of the reaction product and Stoddard solvent together with 1 ml. of water were shaken and centrifuged for 1 hour. No distinct water layer was obtained.

These data show that a separable sludge phase is not produced when the solvent-refined, dewaxed petroleum fraction of the invention is sulfonated.

EXAMPLE XII

(1) A sample of plant balance sulfonate and product oil made according to the procedure of Example I was diluted in sulfonate-free oil to reduce the viscosity and was mixed with a large excess of ethylene glycol. The mixture was stirred for 15 minutes at 100° F. and allowed to stand overnight. Two layers were present with very little coloration in the bottom or ethylene glycol layer. A sample of the top layer was centrifuged, diluted with a small amount of pentane and centrifuged again. The material was then stripped to 300° F. A sample was ashed and compared with an ashed sample of the original blend. The ash content of the original blend was 0.357 wt. percent and the ash content of the treated sample was 0.389 wt. percent indicating that no significant amount of oil was extracted by the ethylene glycol.

(2) A mixture of 158 ml. plant balance of Ca sulfonate and product oil made by SO₃ sulfonation of 250 stock and 158 ml. of isopropyl alcohol was stirred for 30 minutes at about 125° and then allowed to separate at room temperature overnight. The light yellow alcohol layer was decanted and the raffinate was stripped of alcohol by heating. The sulfonate content of the raffinate was 0.513 meq./g. The plant balance product, prior to extraction, had a sulfonate content of 0.488 meq./g.

(3) A mixture of 50 ml. of plant balance product of (2) (sulfonate=0.488 meq./g.) and 80 ml. of 3-pentanone was warmed to effect solution and then allowed to separate. The immiscible layers were present in a ratio of 74 ml. plant balance product solution to 54 ml. ketone solution. The raffinate, on separation and concentration by heating to 420° F., had a sulfonate content of 0.504 meq./g.

This plant balance product raffinate was re-extracted with 8/5 its volume of 3-pentanone. On separation and concentration, the sulfonate content of the plant balance product had increased to 0.515 meq./g.

(4) Equal volumes of plant balance product of (2) and methyl isobutyl ketone form a homogeneous solution.

The above data show that the plant balance product cannot be de-oiled with conventional solvent extraction methods.

EXAMPLE XIII

Calcium petroleum sulfonate was prepared with apparatus such as shown in FIGURE 1 using liquid SO₃ in liquid SO₂. The stabilizer 25 was operated at a temperature of about 280° F. A sample of the product was heated and the vapors evolved were found to be non-acidic at 580° F. but acidic at 590° F. as determined by the acid vapor test. The acid vapor test comprises testing the evolved vapors with moist litmus paper. Base No. =3.6.

A sample of the product was incorporated in a lube oil and subjected to a 480 hour L-1 diesel engine test and the remainder of the product was retreated in stabilizer 25 at a temperature of about 350-360° F. The residence time in the stabilizer was, in each case, about 12 minutes. It is believed that the product was subjected to a temperature of about 360° F. for 10 minutes because subsequent runs have shown that a superior product is obtained if the stabilization or treating step is carried out at a temperature of 360° F. or higher for a period of at least 10 minutes. The retreated product did not evolve acidic vapors at 590° F. Base No. =12.0. A sample of the retreated product was also incorporated in a lube oil and engine tested. The results of the tests are shown in Table XVI.

TABLE XVI

Oil tested	Hours	Top groove carbon rating	Lacquer rating	Over-all rating
280° F. treated.....	480	72	97.6	89.2
360° F. treated.....	480	98	97.6	98.1

About 4 parts by volume per 100 parts of base oil of the plant balance product was used in each lube oil composition. There was some scoring of the piston skirt with the 280° F. oil and none with the 360° F. oil. These data demonstrate the improved stabilization of the product at a temperature of 360° F. or higher.

Recently an improved method has been devised for determining the sulfonate content of the reactor effluent or of the finished product. This method was adapted from that described in "Transactions of the Faraday Society," vol. 44 (1948), page 226, and comprises titrating with cetyl pyridinium bromide.

Preparation and Standardization of Cetyl Pyridinium Bromide Solution

- (1) Dissolve 2±0.1 g. of purified CPB in a liter of water and mix well. Store the solution in a brown, glass-stoppered bottle.
- (2) Add from burets 50.00 ml. of CPB solution and 10.00 ml. of standard 0.1 N potassium dichromate to a 250-ml. beaker.
- (3) Stir the mixture with a stirring rod, cover the beaker with a watch glass and let stand overnight.
- (4) Filter through Whatman No. 40 paper into a 250-ml. Erlenmeyer flask.
- (5) Titrate the filtrate as follows:
 - (a) Add 5 g. of potassium iodide, 4 g. of sodium bicarbonate and 100 ml. of water. Stir until in solution.
 - (b) Add 12 N HCl slowly until carbon dioxide ceases to be evolved. Add 5 ml. excess HCl. Stopper and allow to stand 5 minutes.
 - (c) Titrate with standard 0.1 N sodium thiosulfate until the solution is light yellow in color. Add 1 ml. of starch solution, and titrate until the blue color changes to light green.

(d) Calculate the normality of the CPB solution as follows (Note 1) (Note 2).

$$N = \frac{(DN_d) - (TN_t)}{3V}$$

where:

D =ml. potassium dichromate

N_d =normality of potassium dichromate

T =ml. sodium thiosulfate

N_t =normality of sodium thiosulfate

V =volume of CPB solution

(e) Restandardize the CPB solution at least once per month.

NOTE 1.—In the reaction with CPB the potassium dichromate reacts as a salt, instead of its customary reaction as an oxidizing agent. The factor of 3 in the denominator of the above equation is used to convert the redox normality of the dichromate to its normality as a salt.

NOTE 2.—Discard the CPB solution if it becomes cloudy or any solid material forms in the bottle.

has shown that the residence time which results from intimately contacting the oil and SO_3 produces a satisfactory yield and quality of sulfonate.

EXAMPLE XIV

A solvent-refined and dewaxed oil fraction as described in Example I was continuously sulfonated with liquid SO_3 dissolved in liquid SO_2 under process conditions substantially as described in FIGURE 1. Samples of the reaction produce were taken downstream from the reactor 10 and downstream from time tank 16. The samples were immediately neutralized with a lime water slurry, dried, filtered, stripped and were titrated for sulfonate content using the cetyl pyridinium procedure. The results are shown in Table XVII.

TABLE XVII

Date	Time, p.m.	Composition of slurry, g			Naphtha added after drying, g.	Acid oil in slurry, g.	Sample point	Sulfonate content, meq./g.
		Lime	H ₂ O	Naphtha				
First day----	2:15	60	164	105	450	300	Mix pump.	¹ 0.466
	3:15	60	150	105	500	300	Time tank.	0.479
Second day--	7:18	² 90	² 252	105	450	300	do-----	³ 0.465
	7:23	² 90	235	105	450	300	Mix pump.	0.484

¹ Average of three runs (0.460; 0.468; 0.470).

² This includes 20 g. of lime and 60 g. water added to slurry prior to drying to insure having an excess of alkalinity. Apparently three was more SO_2 in samples taken this date compared to previous day.

³ Average of two runs (0.465; 0.465).

A sample of 0.2 to 0.25 gm. of the material to be tested for sulfonate content is accurately weighed into a glass stoppered flask (50 ml. volumetric). Chloroform is then added to the flask to dilute the material to volume (50 ml.). Then 10 ml. of this solution is pipetted into a 4 oz. square bottle with the portion above the 10 ml. level painted black, 25 ml. of indicator (0.03 gm. methylene blue, 6.5 ml. concentrated H_2SO_4 , 50 gms. sodium sulfate and 940 gms. water) is added and the mixture shaken. The blue color of the indicator migrates almost completely into the chloroform layer. The mixture is titrated with standard cetyl pyridinium bromide until the first green tinge appears in the blue chloroform layer. The number of milliequivalent weights of sulfonate per gram of sample tested is calculated from the following equation:

$$\text{Meq./gm.} = \frac{\text{ml. cetyl pyridinium bromide} \times \text{normality} \times 5}{\text{Wt. of original sample}}$$

*Based on use of a 10 ml. aliquot of the sample diluted in the 50 ml. flask.

Until the cetyl pyridinium bromide procedure was adapted for determining the sulfonate content of the reaction product and the finished product the only accurate method for measuring sulfonate yield was by propane fractionation of the finished product. Pilot plant studies had indicated that a 10 minute quiescent residence time using SO_3 produced a satisfactory product comparable to that produced with a 20-minute, or longer, quiescent residence time. The cetyl pyridinium bromide titration procedure has made possible the testing of the reactor effluent as well as the finished product. A study of residence times

The SO_3 /oil weight ratio during the runs of Table XVII was about 0.075.

The results show that the difference in sulfonate content of the reactor (mix pump) effluent and the time tank effluent is not sufficient to affect appreciably the yield or quality of the product. The reversal in sulfonate content of the reactor and time tank from one day to the next is believed to be due to limits of precision of the analysis and the normal slight fluctuations in flow rates, temperatures, and SO_3 /oil ratios. Thus no significant differences can be detected in the products of the time tank and mix pump. A sulfonate content between about 0.460 and 0.510 meq./g. is satisfactory with respect to quantity and quality of product.

EXAMPLE XV

A sample of the extract oil obtained in preparing a deasphalted, dewaxed and solvent extracted lube oil fraction as described in Example I was extracted with furfural to obtain a raffinate representing a "heart cut" fraction. The extract oil was obtained by the phenol extraction of the deasphalted material remaining after removing SAE 50 lube stock in the propane fractionation of the vacuum still bottoms in refining a topped Mid-Continent crude oil.

The heart cut fraction was sulfonated with 20% fuming sulfuric acid (acid/oil ratio of 0.4) at a temperature of 110° F. The reaction mixture was diluted with four volumes of Stoddard solvent, decanted from sludge which settled, neutralized with an aqueous lime ($\text{Ca}(\text{OH})_2$) slurry, and filtered. The solvent was removed by stripping under vacuum.

The heart cut calcium sulfonate product contained 0.80 meq./gm. of sulfonate.

A carbon black dispersion in toluene was made using the heart cut calcium sulfonate as a dispersion agent.

A carbon black dispersion in toluene was made using an equivalent amount of a calcium sulfonate prepared in apparatus similar to that of FIGURE 1 by the SO₃ sulfonation of 250 stock as described in Example I. This sulfonate product contained 0.49 meq./gm. of sulfonate.

After 16 hours there was no clear separation with either sample. The samples were then shaken and 45 ml. of each was put into clean 50 ml. cylinders containing 5 ml. of water. The samples were shaken and allowed to settle. After 3 hours there was evidence of carbon black settling in the heart cut sulfonate sample. After 3 days settling appeared complete in the heart cut sample but there was no evidence of settling in the 250 stock sulfonate sample.

Lincoln Sequence V Engine tests were conducted using equivalent amounts of sulfonates in the lube oil compositions as shown in the following tabulation.

TABLE XVIII

Run 1		Run 2	
Ingredient	Parts by vol.	Ingredient	Parts by vol.
SAE 10 stock	68.46	SAE 10 stock	70.43
SAE 50 stock	13.00	SAE 50 stock	16.00
250 stock sulfonate	11.50	Heart cut sulfonate	6.53
V.I. improver	4.40	V.I. improver	4.40
Bearing corrosion inhibitor	0.9	Bearing corrosion inhibitor	0.9
Viscosity stabilizer	0.10	Viscosity stabilizer	0.10

Representative results of the Lincoln Sequence V Engine tests are tabulated:

TABLE XIX

	Run 1	Run 2	Perfect
Average sludge rating	44.9	38.4	50.0
Average varnish rating	37.4	35.1	50.0
Piston varnish rating	9.4	8.6	10.0

The data show that the heart cut sulfonate is inferior to the 250 stock sulfonate.

EXAMPLE XVI

Lube oil compositions were prepared containing substantially equal amounts of calcium petroleum sulfonates prepared with oleum (20% fuming H₂SO₄) and with SO₃ dissolved in liquid SO₂. These compositions were then subjected to the Caterpillar L-1 diesel engine test. The results are shown in the following tables:

TABLE XX.—CALCIUM SULFONATE PROCESSING CONDITIONS

	Method	Acid/oil ratio	Reaction temperature, ° F.	Reaction time, minutes
Sulfonate A	Oleum (20% SO ₃ in H ₂ SO ₄)	0.40	135	72
Sulfonate B	SO ₃ in SO ₂	0.08	85	10

TABLE XXI.—LUBE OIL COMPOSITIONS

	Parts by volume	
	A (Oleum)	B (SO ₃)
SAE 10 stock	73.0	72.1
Product oil	5.9	6.1
Plant balance sulfonate	115.9	216.5
Commercial V.I. improver	4.1	4.2
Commercial bearing corrosion inhibitor	0.9	0.9
Commercial viscosity stabilizer	0.1	0.1

¹ Ash=4.94 wt. percent.

² Ash=4.79 wt. percent.

TABLE XXII.—L-1 DIESEL ENGINE TEST RESULTS

	Test hours	Piston cleanliness condition, 100=Clean		
		Top groove carbon rating	Lacquer rating	Over-all rating
Sulfonate A oil	120	98	99.6	99.1
Sulfonate B oil	120	99	99.7	99.5

These data show the similarity of the oleum sulfonated and SO₃ sulfonated products. Other runs including field tests have also shown that the products are similar in beneficial characteristics.

The Caterpillar diesel L-1 test is a very rigorous test and an oil which fails this test can be an excellent lube oil for ordinary use such as in normal private passenger automobile service.

EXAMPLE XVII

Sulfonation of 250 oil of Example I with vaporized or gaseous SO₃, diluted with air, was carried out in an agitated, stainless steel reactor. Agitation was provided by motor-driven dual impellers at 3200 r.p.m. Reaction time was 10 minutes. The sulfonator effluent was neutralized by running it into a tank containing an aqueous lime slurry and Stoddard solvent. The operating conditions for the runs are tabulated below.

TABLE XXIII

Run No.	Oil feed rate, gal./min.	Oil feed temp., ° F.	SO ₃ feed rate, ml./min.	SO ₃ /oil wt. ratio	Reaction temp., ° F.
1 and 2	0.096	110	9.75	0.0575	112
3	0.238	103	17.90	0.0426	130
4	0.195	103	18.60	0.0540	110

Results of analysis of samples from the above runs are shown in the following table. Ash was determined as calcium sulfate and sulfonate was determined by cetyl pyridinium bromide titration.

TABLE XXIV

Run No.	Ash, wt. percent	Sulfonate content, meq./gm.
(1) Effluent product	1.13	0.025
(2) Reactor sample	0.64	0.012
(3) Effluent product	1.87	0.103
(4) Effluent product	2.19	0.124

The low values of ash and sulfonate content indicate that the yield of sulfonate is too low for the process to have any practical value.

EXAMPLE XVIII

A 9.1 kg. sample of 250 oil, as described in Example I, was diluted with 3,000 ml. of ethylene chloride and sulfonated at 110° F. with 1.82 kg. of liquid SO₃ as an ethylene chloride complex with 2,000 ml. of ethylene chloride.

Of the 45.6 acid equivalents of SO₃ added, 26.4 equivalents were found by titration of an aliquot of the reaction mass. An iodometric titration of the reaction products disclosed 1.45 percent SO₂ or 7.76 acid equivalents. Total acidity corrected for SO₂ was 18.64 equivalents.

The reaction product was extracted with water in a counter-current water extraction operation conducted in a spinning band column with a continuous water phase. Four batchwise stages of extraction were utilized. The sulfonic acid of the 250 oil is water insoluble. Titration of the stripped, water washed product, weighing 8.05 kg., indicated 2.07 acid equivalents remained or 8 percent of the original titratable acidity.

Six kilograms of the water washed product, stripped of solvent, was neutralized with 176.5 grams of guanidine carbonate. Actual and calculated values for the nitrogen content of the finished product agreed within 0.03 percent. Nitrogen found by the Kjeldahl method was 1.26 percent whereas the calculated value, base on the amount of guanidine added, was 1.29 percent. The value of 1.26 percent nitrogen is calculated to be equivalent to 2.4 weight percent calcium sulfate ash by substituting calcium for guanidine.

Reasonable variations and modifications are possible within the scope of the disclosure of the present invention, the essence of which is the provision of an improved process for producing metal petroleum sulfonates and in the discovery that the associated product oil resulting from the sulfonation process provides a superior lube oil base stock with respect to reducing octane requirement increase characteristics.

That which is claimed is:

1. A process for producing superior lubricating oil additives which comprises intimately admixing a quantity of sulfonating agent consisting essentially of liquid SO_3 dissolved in an inorganic solvent equivalent to from 0.2 to 1 part by weight of 20 percent fuming sulfuric acid and 1 part by weight of a propane-fractionated, solvent-extracted and dewaxed intermediate base bright stock of about 200 to 230 SUS at 210°F . and having a viscosity index of at least about 85, at a temperature of about 50 to about 200°F .; neutralizing the resulting reaction product with at least the minimum required for neutralization of an aqueous slurry of a basic alkaline earth metal compound; heating the mixture in liquid phase at a temperature in the range of about 360 to 400°F . for about 10 minutes to render same noncorrosive; vaporizing and removing water from said mixture; and removing inorganic solids so as to recover a mixture of alkaline earth petroleum sulfonate and product oil having a sulfated ash content of not more than 6 weight percent.

2. The process of claim 1 wherein the sulfonating agent to oil weight ratio in the sulfonation step is equivalent to a 20 percent fuming sulfuric acid to oil ratio of about 0.3:1 to about 0.6:1.

3. The process of claim 1 wherein the sulfonating agent is SO_3 dissolved in SO_2 and the SO_3 to oil weight ratio in the sulfonation step is equivalent to a 20 percent fuming sulfuric acid to oil ratio of about 0.3:1 to 0.6:1.

4. The process of claim 1 wherein the sulfonating agent is 20 percent fuming sulfuric acid, the acid to oil weight ratio in the sulfonation step is about 0.3:1 to about 0.6:1 and the mixture of sulfonating agent and bright stock is maintained in a reaction zone at reaction temperature and with a minimum of mixing for a total reaction period of 20 to 90 minutes.

5. A process for producing a superior lubricating oil blending stock which comprises admixing a quantity of sulfonating agent consisting essentially of liquid SO_3 dissolved in an inorganic solvent equivalent to from about 0.1:1 part by weight of 20 percent fuming sulfuric acid and 1 part by weight of a propane-fractionated, solvent-extracted and dewaxed intermediate base bright stock of about 200 to 230 SUS at 210°F . and having a viscosity index of at least about 85 at a temperature in the range of 50 to 200°F .; neutralizing the resulting reaction mixture with at least the minimum amount required for neutralization of an aqueous slurry of an alkaline earth metal hydroxide; heating the aqueous slurry to a temperature of 360 to 400°F . for about 10 minutes; removing water and inorganic solids to obtain a neutralized sulfonation product containing not more than 6 weight percent sulfated ash; and extracting the total neutralized sulfonation product with propane at a pressure of 600 to 700 p.s.i.g. at a temperature of 150 to 190°F . to remove sulfonates and to recover sulfonate-free oil having a sulfated ash content of less than 0.2 weight percent as the blending stock product of the process.

6. The process of claim 1 wherein the hydrocarbon fraction has a viscosity of about 200 SUS at 210°F . and the sulfonation temperature is in the range of 130 to 150°F .

7. A process for producing superior lubricating oil compositions which comprises admixing 20 percent fuming sulfuric acid and a propane-fractionated, solvent-extracted and dewaxed intermediate base bright stock of about 200 to 230 SUS at 210°F . and having a viscosity index of at least about 85; passing said mixture to a reaction zone maintained at a temperature of 50 to 200°F . for a total reaction period of 20 to 90 minutes with a minimum of mixing; neutralizing the resulting reaction mixture with at least the minimum required for neutralization of a slurry of an alkaline earth metal hydroxide and water; heating said slurry to at least 360°F . for at least about 10 minutes to render the products noncorrosive; heating to remove water vapor and to reduce water content to about 0.1 weight percent; removing inorganic solids; recovering a mixture of alkaline earth metal petroleum sulfonate and product oil having a sulfated ash content of not more than 6 weight percent, adding a first portion of said mixture of sulfonate and product oil to a refined lubricating oil base stock; and adding additional product oil obtained by extracting a second portion of said mixture of sulfonate and product oil with propane at a pressure of 600 to 700 p.s.i.g. and a temperature of 150 to 190°F . and having a sulfated ash content of less than 0.2 weight percent in an amount up to the amount of product oil in said mixture of sulfonate and product oil.

8. A process according to claim 7 wherein a ketone diluent is added to the slurry prior to removing inorganic solids and the amount of alkaline earth in the slurry is between the minimum required for neutralization and 1.25 times said minimum.

9. A process according to claim 7 wherein the mixture of sulfonate and product oil recovered from the sulfonation process has an ash content of about 4.5 to 5.5 weight percent.

10. A process for producing superior lubricating oil additives which comprises intimately admixing at a temperature in the range of about 50 to 200°F . about 0.02 to 0.2 part by weight of liquid SO_3 , as liquid SO_3 dissolved in an inorganic solvent with 1 part by weight of a propane-fractionated, solvent-extracted and dewaxed intermediate base bright stock of about 200 to 230 SUS at 210°F . and having a viscosity index of at least about 90; neutralizing the resulting reaction product with at least the minimum required for neutralization of an aqueous slurry of calcium hydroxide; heating the mixture in liquid phase at a temperature in the range of about 360 to 400°F . for about 10 minutes to render same noncorrosive; vaporizing and removing water from said mixture; diluting the mixture with a liquid hydrocarbon; and removing inorganic solids so as to recover a mixture of calcium sulfonate and product oil having a sulfonated ash content of not more than 6 weight percent and having a base number greater than 7.

11. The process of claim 10 wherein liquid SO_3 is dissolved in liquid SO_2 , the liquid SO_3 to oil weight ratio in the sulfonation step is about 0.06 to 0.12.

12. The process of claim 10 wherein the liquid SO_3 is dissolved in liquid sulfuric acid and the mixture of SO_3 dissolved in liquid sulfuric acid and bright stock is maintained in a reaction zone at reaction temperature with a minimum of mixing for about 20 to 90 minutes.

13. A lubricating oil additive comprising a mixture of calcium petroleum sulfonate and the unsulfonated residual oil associated therewith which mixture is obtained by sulfonating at a temperature of about 50 to 200°F ., 1 part by weight of a propane-fractionated, solvent-extracted, and dewaxed intermediate base bright stock having a viscosity of about 200 to 230 SUS at 210°F . and a viscosity index of at least about 90, with about 0.02 to 0.2 part by weight of liquid SO_3 dissolved in liquid SO_2 ; neu-

tralizing the resulting reaction product with at least the minimum required for neutralization of an aqueous slurry of calcium hydroxide; heating the mixture in the liquid phase at a temperature in the range of about 360 to 400° F. for about 10 minutes; and removing water and inorganic solids therefrom to obtain a lubricating oil additive containing not more than 6 weight percent sulfated ash.

14. A lubricating oil composition comprising a petroleum lubricating oil base stock containing about 0.2 to 30 weight percent of the plant balance product obtained by sulfonating a propane-fractionated, solvent-extracted, dewaxed intermediate base bright stock having a viscosity of about 200 to 230 SUS at 210° F. and a viscosity index of at least about 90 with liquid SO₃ dissolved in liquid SO₂ in a ratio of SO₃ to oil of about 0.06 to 0.12 at a temperature in the range of about 50 to 200° F., neutralizing the resulting reaction mixture with at least the minimum required for neutralization of an aqueous slurry of calcium hydroxide; heating the resulting mixture in liquid phase at a temperature of about 360 to 400° F. for about 10 minutes; and removing water and inorganic solids therefrom to obtain a plant balance product containing not more than 6 weight percent sulfated ash.

15. The composition of claim 14 wherein the base stock contains about 3 to 20 weight percent of the plant balance product.

16. The process of claim 11 wherein the mixture is diluted with a liquid hydrocarbon prior to removal of solids therefrom.

17. A lubricating oil composition comprising a petroleum lubricating base stock containing about 0.1 to 15 weight percent of a calcium petroleum sulfonate prepared by sulfonating a propane-fractionated, solvent-extracted, dewaxed intermediate base bright stock having a viscosity of about 200 to 230 SUS at 210° F. and a viscosity index of about 90 with liquid SO₃ dissolved in liquid SO₂ in a ratio of SO₃ to oil of about 0.02 to 0.2 at a temperature in the range of about 50 to 200° F.; neutralizing the resulting reaction mixture with at least the minimum required for neutralization of an aqueous slurry of calcium hydroxide; heating the resulting mixture in the liquid phase at a temperature of about 360 to 400° F. for about 10 minutes; and removing water and inorganic solids therefrom to obtain calcium petroleum sulfonate containing not more than 6 weight percent sulfated ash.

18. A process for producing superior lubricating oil additives which comprises intimately admixing a quantity of sulfonating agent consisting essentially of liquid SO₃ dissolved in liquid SO₂ equivalent to from about 0.3 to 0.6 part by weight of 20 percent fuming sulfuric acid and 1 part by weight of a propane-fractionated, solvent-ex-

tracted and dewaxed intermediate base bright stock of about 200 to 230 SUS at 210° F. and having a viscosity index of at least about 85, at a temperature of about 50 to about 200° F.; neutralizing the resulting reaction product with at least the minimum amount required for neutralization of an aqueous slurry of a basic alkaline earth metal compound; heating the mixture to a temperature in the range of about 360 to about 400° F. for about 10 minutes to render same noncorrosive; vaporizing and removing water from said mixture; removing inorganic solids to obtain a mixture containing not more than 6 weight percent sulfated ash; recovering oil from said mixture by extraction with propane at a pressure of 600 to 700 p.s.i.g. and a temperature of 150 to 190° F. as a superior lubricating oil additive; and recovering the resulting alkaline earth metal petroleum sulfonate as an additional superior lubricating oil additive.

19. A process for producing superior lubricating oil additives which comprises intimately admixing, at a temperature in the range of about 50 to 200° F., a quantity of sulfonating agent consisting essentially of liquid SO₃ dissolved in liquid SO₂ equivalent to from about 0.1 to 1 part by weight of 20 percent fuming sulfuric acid with 1 part by weight of a propane-fractionated, solvent-extracted and dewaxed intermediate base bright stock of about 200 to 230 SUS at 210° F. and having a viscosity index of at least about 85; neutralizing the resulting reaction product with at least the minimum amount required for neutralization of an aqueous slurry of a basic alkaline earth metal compound; heating the mixture to a temperature in the range of about 360 to about 400° F. for about 10 minutes to render same noncorrosive; vaporizing and removing water from said mixture; removing inorganic solids to obtain a mixture containing not more than 6 weight percent sulfated ash; recovering oil from said mixture by extraction with propane at a pressure of 600 to 700 p.s.i.g. and a temperature of 150 to 190° F. as a superior lubricating oil additive; and recovering the resulting alkaline earth metal petroleum sulfonate as an additional superior lubricating oil additive.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,135,693

June 2, 1964

William B. Whitney et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 22, line 56, for "sulfonated" read -- sulfated --;
column 23, line 27, for the claim reference numeral "11"
read -- 1 --.

Signed and sealed this 10th day of November 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

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