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LUBRICANTS

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1

This invention relates to improved lubricants. In one embodiment it relates to new gelation agents and their preparation, and to their use in the manufacture of ashless greases. In another embodiment this invention relates to improved lubricating oils. In another embodiment it relates to the manufacture and use of new additive materials in lubricating oils. In still another embodiment it relates to the reduction of the deposition and accumulation of sludge on oil lubricated engine parts, in an engine system. This application is a continuation-in-part of our copending application Serial No. 44,575, filed August 16, 1948.

In the manufacture of lubricants, a great many substances have been used as gelation agents. These materials are incorporated with mineral oils under the proper conditions to produce lubricants and lubricating greases. The most common among these gelation agents are the sodium, calcium, and aluminum salts of the higher molecular weight fatty acids. Certain other metal salts of fatty acids have also been used, however much less frequently. In some instances, mahogany acids have been used in place of the fatty acids. Such mahogany acids are the result of the action of sulfuric acid on petroleum oils, and their composition varies widely depending on the oil treated, and conditions of treatment, and the volume and strength of sulfuric acid used. Usually they are used in the form of their sodium or calcium salts.

Salts of the fatty acids and mahogany acids just described are often called gelation agents. It is one of their properties that when added to oils of the proper type and under certain conditions they will cause gelling and thickening of the oils, making them have utility as lubricants and lubricating greases.

At the present time it is common practice to enhance or modify certain of the properties of lubricating oils through the use of various additives or improvement agents. The lubricating oils employed in internal combustion engines, such as automotive, light aircraft, and diesel engines in particular, require the use of additive agents to render them serviceable under the adverse environmental conditions encountered in these engines. Among the various additives employed in modern engine oils, one of the most important is the type which acts to prevent accumulation of sludge in the crankcase and on the cylinder walls, thereby preventing sticking of the piston rings, and the formation of varnish-like coating on the pistons and cylinder walls. Because of their general function of maintaining a clean engine, additives of this nature are termed "detergents," although it is now understood that they have little utility in cleaning a dirty engine but by virtue of dispersant activity prevent or greatly retard engine fouling.

It has long been recognized that ash content

2

of detergents and other additives in a lube oil employed in engine operation contributes to upper cylinder deposits which in turn contribute to and predispose toward pre-ignition, valve burning, and general rough engine operation. The use of ash-forming detergent additives in engine operation, is for these reasons, often inadvisable, particularly in aircraft engines. Our invention is concerned with new and novel ashless oil detergents, and with improved lubricating oil containing such detergents.

It is an object of our invention to provide improved lubricants. Another object is to provide improved lubricating greases. Another object is to provide improved lubricating oils. Another object is to provide additive agents for imparting improved properties to lubricating oils. Another object is to provide gelation agents, and for their manufacture, and for their use in the manufacture of ashless greases. Another object is to provide ashless lubricating oil detergents. Another object is to provide a method for the manufacture of new and improved lubricating oil detergents of the sulfonate type. Another object is to provide a method for preventing an accumulation of oil degradation products on oil lubricated engine parts. Other objects will be apparent to those skilled in the art from the accompanying discussion and disclosure.

In accordance with a broad embodiment of our invention we have provided improved ashless lubricant compositions comprising mineral oils incorporated with a guanidine salt of an organic sulfonic acid selected from the group consisting of synthetic guanidine alkyl aryl sulfonates and guanidine petroleum sulfonates, and containing from 0.1 to 60 weight per cent of the guanidine salt.

The term "lubricant" is used herein to denote not only a lubricating grease but also a lubricating oil, and includes compositions formed by incorporating a guanidine sulfonate of the type described above with a mineral oil.

We have discovered that certain alkyl aryl sulfonic acids can be neutralized with guanidine or a basic guanidine salt to form guanidine alkyl aryl sulfonates. Certain of these new and novel guanidine alkyl aryl sulfonates disperse readily in mineral oil as gelation agents to form improved greases of the ashless type, while certain others of relatively high molecular weight are oil-soluble and when dissolved in a lube oil base stock impart valuable detergent properties to it thus, forming improved lubricating oils. We have further discovered that certain petroleum sulfonic acids can be neutralized with guanidine or a basic guanidine salt and that certain guanidine petroleum sulfonates thus produced are oil-soluble, and when dissolved in a base lube oil stock impart valuable detergent properties to it. Additionally, as described hereafter, other guanidine petroleum sulfonates differing from the

detergent types principally in molecular weight and degree of sulfonation have pronounced gelling tendencies when dispersed in oil and may be utilized to advantage in the preparation of greases.

The guanidine alkyl aryl sulfonates as grease gelation agents contain from 17 to 35 carbon atoms in the molecule, although certain of these serve also as detergents in oil systems, dependent to a large degree upon the concentration of the guanidine salt added, particularly those formed from alkyl aryl sulfonic acids containing at least 24 carbon atoms per molecule. However, when we employ guanidine alkyl aryl sulfonates as oil detergents, we prefer to employ those formed from alkyl aryl sulfonic acids containing from about 40 to 70 carbon atoms per molecule or higher. When employing our novel guanidine petroleum sulfonates as oil detergents, we employ those formed from petroleum sulfonic acids containing at least 40 carbon atoms in the molecule.

In forming our lubricating grease compositions we disperse the guanidine alkyl aryl sulfonate in a mineral oil base stock to form a composition containing from 5 to 60 weight per cent of the guanidine alkyl aryl sulfonate.

The alkyl aryl sulfonic acids, which on combining with guanidine form our gelation agents, may be produced by the alkylation of an aromatic nucleus such as benzene, naphthalene, diphenyl, or anthracene, or their alkyl derivatives, with olefins which boil in the approximate range of 190 to 315° C. When alkylating alkyl aromatics such as, for example toluene or xylene, a fraction of olefins in the 190 to 315° C. range must be selected so that after alkylation, the total number of carbon atoms in the alkyl groups is not more than about 20. The preferred boiling range of the alkylating olefins is usually 190 to 315° C. and such olefins generally contain from about 10 to 20 carbon atoms per molecule, however, a narrower range of, say 230 to 250° C., may often be desirable and is quite satisfactory. Straight chain olefins having the double bond in the "one" position are well suited for use in our invention. Branched chain olefins are also quite applicable. It is to be noted, however, that a branched chain olefin containing the same number of carbon atoms as a straight chain olefin acts as a straight chain olefin containing less carbon atoms insofar as oil-solubility is concerned.

A suitable gelation agent is a guanidine salt of an alkyl aryl sulfonic acid in which the alkyl group contains at least 10 carbon atoms. When there are more than ten carbon atoms present in the alkyl groups, a satisfactory gelation agent is one with at least one alkyl group containing 10 carbon atoms. Another satisfactory salt or gelation agent is a guanidine alkyl aryl sulfonate having two alkyl groups having at least 8 carbon atoms each. Another is one having three alkyl groups of at least 6 carbon atoms each. Generally speaking, when only one alkyl group is present in the guanidine alkyl aryl sulfonate, it should contain at least 10 carbon atoms, and no matter how many alkyl groups are present they should preferably contain a total of not more than about 20 carbon atoms.

The above described guanidine alkyl aryl sulfonates having utility both as gelation agents and as oil detergents, and the guanidine petroleum sulfonates described more fully hereinafter are new compounds.

Any conventional method is suitable for alkylating aromatics with olefins to produce alkyl aro-

maties for sulfonation and subsequent neutralization in the preparation of our synthetic guanidine alkyl aryl sulfonates. Such a method may employ sulfuric acid, hydrofluoric acid, or boron trifluoride as catalyst for the alkylation; however, the invention is not to be limited by the particular means used for alkylating aromatics. Other methods for obtaining alkyl aromatics, such as alkylation of aromatics with alcohols, alkyl halides, ethers, or esters, are well suited for our invention. Suitable alkylatable aromatics are those containing only one ring such as benzene, toluene, and xylene as mentioned above. Satisfactory results may also be obtained from multiring compounds, in particular naphthalene, diphenyl, anthracene, and their lower alkyl homologues. It is generally preferred that not more than three rings be present in the aromatic hydrocarbon. The compounds, alkylated with olefins as described above, are then sulfonated by suitable means, such as by fuming sulfuric acid, as is well known to those skilled in the art, to produce alkyl aryl sulfonic acids. However, our process is not to be limited by the means of sulfonation employed. These latter compounds are then combined with the strong organic base guanidine to form a gelation agent which is the guanidine salt of the sulfonic acid. Usually this material may be used to thicken an oil and to obtain a lubricant having the form of a solid or semisolid cake, but in special cases where extremely light lubricants are desirable, the final lubricant mixture may be in the form of a liquid, usually being thick and having a texture similar to syrup or honey. When referring to the neutralization of the alkyl aryl sulfonic acid with a guanidine compound in either the specification or the claims, we mean to include also the use of guanidine by itself.

One specific method for the preparation of one of our novel guanidine alkyl aryl sulfonates is as follows. A suitable alkyl aryl sulfonic acid having the requisite number of alkyl carbon atoms as described above, is dissolved in a low-boiling alcohol such as, for example isopropyl alcohol or butyl alcohol. To the thus-formed solution is added a molar excess of a concentrated aqueous solution of a guanidine compound, suitably the carbonate. The solution separates into an alcohol layer containing the guanidine alkyl aryl sulfonate and a water layer. It is preferable not to use an alcohol boiling below isopropyl alcohol because inadequate separation of the alcohol layer from the water layer is obtained. The alcohol layer is removed by suitable means, such as decanting, and then filtered to remove any solid material, after which it is evaporated to recover the guanidine alkyl aryl sulfonate. If no solid material is present in the alcohol layer, it may be evaporated directly without filtering. For further purification (if desired) the guanidine sulfonate may be extracted with anhydrous alcohol, the alcohol then being evaporated.

In order to make an improved grease in accordance with our invention, the novel guanidine alkyl aryl sulfonate already described is admixed with a mineral oil of suitable properties such as viscosity, density, flash and fire, pour-point, specific gravity, color, and specific dispersion, chosen in accordance with the type of grease desired. Generally 5 to 60 weight per cent of the salt is adequate and it is often preferred to use 15 to 50 weight per cent. Ranges of properties which cover oils suitable for use in making lubricants in accordance with our invention are given in the

following table. Broadly, an oil with some lubricating properties is desirable and may have a viscosity in the range of 50 to 700 SUS @ 100° F., but may go as high as 2000-4000 SUS @ 100° F. It is preferable that the viscosity index of the oil be above 60, although lower viscosity index oils may be used. More narrow and preferred ranges for the mineral oil are the following:

Viscosity, SUS at 100° F.-----	125-500
Refractive index, N_D^{20} -----	1.4700-1.4920
Specific gravity D_4^{20} -----	0.8400-0.8890

Usually it is necessary to heat the salt and oil so that the salt becomes a liquid and will disperse throughout the oil, i. e., to a temperature above the melting point of the gelation agent to insure a homogeneous mixture of components. Care must be taken, however, not to heat the mixture to such a temperature that decomposition of the particular salt used takes place. The temperature to which it will be necessary to heat the oil and salt will be readily discernible to one skilled in the art of grease making. After admixing the salt and mineral oil at an elevated temperature, the mixture is cooled by suitable means. It is preferable to chill the grease rapidly, that is, bring it to room temperature within a period of about 10 minutes or less. Following such cooling, the material is milled to a smooth grease. Grease milling is ordinarily considered as a simple process for smoothing out and obliterating the clots or lumps of heavy grease formed by chilling. Suitable apparatus for such processing are stone buhr mills and the like.

Conventional grease manufacturing equipment frequently may be utilized for the practice of our invention; however, the invention is not to be limited by any particular type used. For example, a jacketed kettle through which may be circulated a heat transfer material is satisfactory for dispersing the gelation agent in the oil. At times, it may be desirable to pass a coolant through the jacket so that the mixture may be cooled quickly once the proper amount of gelation agent has been dispersed. In cases of higher concentration, discharge of the dispersion and external cooling may be necessary due to the firm texture of the cooled mass. It is often advantageous to use mechanical stirring means because by so doing the time of manufacture is greatly reduced.

As stated above we have found that certain guanidine petroleum sulfonates can be utilized as gelation agents in the manufacture of greases. Those guanidine petroleum sulfonates are formed from petroleum sulfonic acids containing from 20 to 40, preferably from 22 to 35, carbon atoms in the molecule, and can be prepared by the sulfonation of a lube oil stock of SAE 10 or 20 grade followed by neutralization of the sulfonate formed with guanidine or a guanidine basic salt. We have found that in preparing the guanidine petroleum sulfonate gelation agents in this matter, some oil-soluble guanidine sulfonates may be formed. However it is generally unnecessary to remove these oil-soluble sulfonates for use of the guanidine sulfonate product as a gelation agent. We have also found that by sulfonating a heavy petroleum fraction, say as high as one containing 70 to 80 carbon atoms in the molecule and by neutralizing di- or polysulfonic acids thus formed, with guanidine, the resulting polyguanidine sulfonates are excellent gelation agents, and have such a molecular weight that the molecule contains one sulfonate group per 20 to 35 carbon atoms.

In accordance with one embodiment of our invention we have provided improved oil compositions comprising lubricating oils and from 0.1 to 25 weight per cent of an oil-soluble guanidine salt of an organic sulfonic acid, as an ashless oil detergent, selected from the group consisting of synthetic guanidine alkyl aryl sulfonates and guanidine petroleum sulfonates. Higher concentrations of active ingredient may be used insofar as they are compatible with viscosity requirements and economics.

In another embodiment of our invention we provide a method for preventing accumulation of sludge and associated deteriorative oil reaction materials on oil-lubricated engine parts by incorporating with the lubricating oil as an ashless detergent an oil-soluble guanidine salt of the type described above.

In another embodiment we provide a method for the manufacture of the oil-soluble detergents described above.

In the preparation of ashless detergents of the sulfonate type the employment of derivatives of ammonia as the cationic portion of the molecule is one approach. However, in the conversion of the petroleum sulfonic acids of commerce to ashless lube oil detergents, the requirements of good thermal stability and resistance to hydrolysis tend to discourage ammonia, amines and ordinary quaternary bases such as tribenzyl methyl ammonium hydroxide and the like. On the other hand, the imide of urea, guanidine, is a strong base, and while unstable in the form of the free base, it exhibits a high degree of thermal and hydrolytic stability in the form of its salts of strong acids and to a lesser extent as salts of weak acids. As discussed herein and shown in our aforementioned copending application, guanidine salts of certain synthetic alkyl aryl sulfonic acids of moderate molecular weight are quite useful as thickening agents in the preparation of greases. Likewise, we have found that certain guanidine salts of commercially available petroleum sulfonic acids exhibit gel-forming tendencies, when associated with mineral oils, detrimental to their application as lubricating oil detergents. In general the unfavorable solubility relationships of guanidine sulfonates necessitate special selection of species and special treatment prior to their application in lubricating oils where excessive deviation from true solutions cannot be tolerated.

We have now discovered that oil-soluble guanidine salts of petroleum sulfonic acids can be formed by careful selection of sulfonation stocks and by appropriate refining of the crude sulfonic acids and/or guanidine sulfonates. We have further found that the certain oil-soluble and ash-free guanidine sulfonates of this invention when dissolved in oil provide excellent detergency in the operation of internal combustion engines.

The hydrocarbon raw materials for production of oil detergents of this invention may be of synthetic or petroleum origin although the latter are preferred for economic reasons. In the case of synthetic sulfonation stocks alkylated aromatics of about 24 carbon atoms represent the approximate lower limit of useful guanidine alkyl aryl sulfonates from the oil solubility standpoint. Since guanidine sulfonates even in this molecular weight range exhibit somewhat limited solubility in lubricating oil, we prefer to employ synthetic hydrocarbon sulfonation stocks of about 40 carbon atoms per molecule and higher to insure additive solubility in all concentrations

and in various types and viscosity grades of oil. In the case of naturally occurring petroleum sulfonation stocks, adequate oil solubility of the guanidine sulfonates can only be realized from bright stock fractions having at least 40 carbon atoms per molecule with most favorable results being obtained with oils having from 50 to 70 carbon atoms per molecule.

In the practice of one embodiment of our invention, the following steps are involved in the manufacture of our guanidine petroleum sulfonate ashless detergents: (1) sulfonation; (2) neutralization of the sulfonic acid formed, with guanidine; (3) separation of oil and oil-soluble additive from gel-forming oil-insoluble components; and (4) preparation of additive-oil solutions of known concentration. In the case of synthetic hydrocarbons such as alkylated aromatics, conventional sulfonation techniques may be applied as already discussed.

When employing our preferred solvent-extracted bright stocks in the preparation of our guanidine petroleum sulfonate detergents, anhydrous SO_3 dissolved in ethylene chloride is the sulfonation agent of choice since such hydrocarbons are resistant to fuming acid and because the more potent SO_3 produces a rapid clean cut sulfonation reaction with virtually no formation of acid sludge. The crude sulfonation product may be subjected to purification as such, or it may be directly neutralized with aqueous guanidine or preferably guanidine carbonate. In the former case, the crude sulfonation reaction mixture is extracted with water to remove inorganic acids thus conserving guanidine in the neutralization step to follow. The sulfonic acids are thereafter extracted from the washed reaction mixture with an alcohol of 1 to 6 carbon atoms such as isopropyl alcohol. The alcoholic solution, i. e., extract, is then neutralized with a suitable guanidine derivative. An alcohol-insoluble portion separating on neutralization and which contains the desired product is repeatedly extracted with alcohol until all oil-insoluble sulfonates have been removed. Molecular weight determination and quantitative nitrogen assay on this material provide a convenient means of computing the final sulfonate concentration. If the crude sulfonation reaction product is directly neutralized without purification, the crude neutralized sulfonation product, i. e., the mixture of oil and guanidine monosulfonates, polysulfonates, sulfate, sulfite and carbonate, is washed with water to remove sulfate, sulfite, carbonate, and some polysulfonates, and the purified residue is then extracted with an alcohol of 1 to 6 carbon atoms per molecule at about 70 to 75° F. in order to remove oil-insoluble guanidine sulfonates.

Ordinarily the extraction of the neutralized petroleum sulfonic acid is completed on reduction of the nitrogen content to about 1.0 to 1.5 per cent which provides an oil concentrate having a nominal sulfonate content of about 20 to 25 percent active ingredient. Since in many cases the unreacted carrier oil may have an undesirable high viscosity, it is often advantageous to carry out an exhaustive fractional extraction thus completely denuding the carrier oil of its sulfonate content and utilizing those sulfonate fractions showing complete oil solubility in preparing the final assayed and diluted additive.

The purification of the petroleum guanidine sulfonates is an important feature of the present invention since the total petroleum guanidine

sulfonates formed are found by engine tests to be not only devoid of demonstrable detergent activity, but actually to contribute to overall engine sludge and varnish. While the alcohol extraction step referred to hereinbefore apparently serves to segregate oil-soluble from oil-insoluble guanidine sulfonates other effects may be operative and pertinent to the ultimate effectiveness of our novel detergents.

One method by which an oil-soluble guanidine alkyl aryl sulfonate detergent of our invention can be prepared comprises the conventional alkylation of an aromatic hydrocarbon such as benzene, naphthalene, diphenyl, or anthracene, or their alkyl derivatives, with an olefin of a molecular weight selected so that the resulting alkylate contains at least about 24 carbon atoms per molecule, and preferably from 40 to 70 carbon atoms or even higher. Suitable olefins may include decene, octadecene, triacontene and the like or commercial mixtures of such olefins. In most instances more than one alkyl group is introduced into the aromatic nucleus in order to arrive at a sulfonation stock of adequate molecular weight. The resulting alkylate is then sulfonated employing any suitable sulfonating agent such as fuming sulfuric acid, sulfur trioxide, or the like, and the sulfonic acid thus formed is reacted with guanidine or a basic salt of guanidine, as for example guanidine carbonate, to form a guanidine alkyl aryl sulfonate detergent of our invention.

One procedure for carrying out this latter reaction comprises dissolving an alkyl aryl sulfonic acid, formed as indicated above, in a lower boiling alcohol as a solvent, as for example isopropyl alcohol or butyl alcohol. To the thus formed alcohol solution is added a stoichiometric excess of a concentrated aqueous solution of a guanidine compound, preferably the carbonate. The resulting reaction solution separates into a solvent layer containing the guanidine alkyl aryl sulfonate, and a water layer. It is preferable to use an alcohol as a solvent containing at least 3 carbon atoms in the molecule since inadequate separation of the alcohol and water layers otherwise occurs. The alcohol and water layers are then separated, as for example by decantation, and the alcohol is removed from the solvent layer by vaporization to provide the desired guanidine alkyl aryl sulfonate detergent material. In some cases solid materials may be present in the solvent layer, in which case it is desirable to filter the layer and then vaporize the alcohol solvent from the filtrate.

In a more specific embodiment of our invention relating to the manufacture of oil-soluble and ash-free guanidine petroleum sulfonates having exceptional lube oil detergent properties, a sulfonation base stock is selected from the more viscous or bright stock fractions of petroleum. More specifically we prefer to employ a deasphalted and solvent refined petroleum fraction having a viscosity range between about 80 and 700 SUS @ 210° F. A preferred sulfonation stock is a propane-fractionated, solvent-extracted and dewaxed Mid-Continent oil of about 200 to 230 SUS @ 210° F. having a viscosity index of about 85 to 95 or higher. Similar bright stocks of Pennsylvania or naphthenic origin while less desirable may be used. It will be appreciated by those skilled in the art that by the term "propane-fractionated" is meant fractionation of the oil or bright stock with propane to effect deasphaltization and also separation of oil components on

basis of viscosity and that by "solvent refining" is meant the removal by solvent extraction of the more highly aromatic fractions from the deasphalted bright stock. In the latter step any suitable selective solvent can be employed, among which are included phenol, cresylic acids, chlorinated ethers such as chloroethyl ether, nitrobenzene, furfural, and the like. The deasphalted and solvent refined oil is generally dewaxed prior to sulfonation although dewaxing can be dispensed with if complete segregation of sulfonic acids from the waxy oil is carried out at temperatures above the solution temperature of the wax. In any case prior deasphalting and extraction is definitely required. In general, lube stocks lighter than about 80 SUS @ 210° F. are unsatisfactory for use in the manufacture of our lubricating oil detergents since the resulting guanidine petroleum sulfonates are not sufficiently soluble in oil to serve as detergent additives.

A feature of our success in sulfonating the high molecular weight oils of this invention is the employment of stabilized liquid sulfur trioxide as the sulfonating agent. Our procedure for sulfonating with this reagent is well known in the art and involves dissolving the anhydrous liquid SO₃ in from 2 to 5 times its weight of dry ethylene chloride to provide an easily manipulated sulfonation reagent. The hydrocarbon sulfonation stock may likewise be dissolved in ethylene chloride or any other suitable non-reactive solvent such as carbon tetrachloride, chloroform, pentane, hexane, or the like.

Sulfonation in a preferred embodiment can be carried out in a continuous flow system or in batch agitators. In either case the quantity of SO₃ added is ordinarily adjusted to give a molar ratio of SO₃ to sulfonation stock of between about 1:1 and 3:1. The reaction between the hydrocarbon and SO₃, even in the case of extremely viscous bright stocks having molecular weights in the range of 800 to 900, is very rapid and exothermic. Sulfonation temperatures are ordinarily controlled within the range of about 50 to 200° F. with a preferred operating range between 80 and 130° F. Lower temperature may be employed without seriously slowing down reaction rates, but no particular advantage accrues therefrom. At temperatures above about 200° F. excessive oxidation with liberation of sulfur dioxide occurs.

On completion of the sulfonation reaction sufficient aqueous guanidine carbonate solution is added to bring both the oil and water phases to a pH value within the range of 8 to 8 as determined on a pH meter. The aqueous phase is separated and water-soluble reaction products such as guanidine sulfate, sulfite, carbonate and certain polysulfonates are washed from the oil phase with water or water containing some isopropyl alcohol if serious emulsion difficulties are encountered. Separation of oil-insoluble sulfonates is accomplished by extracting the water-washed oil solution and/or dispersion with an anhydrous alcohol. We have found that petroleum sulfonates of poor oil solubility characteristics are more soluble in anhydrous alcohols such as isopropyl alcohol than are the oil-soluble sulfonates. Since the guanidine petroleum sulfonates are strongly surface-active, emulsion formations can be avoided in this extraction step by dissolving the oil sulfonate mixture in an equal volume of hot alcohol, i. e. above 100° F. and as high as 150° F. or higher, as for example at its boiling point, and then slowly cooling to room temperature, e. g., to below about 100° F. followed by

separation of the alcoholic phase. We have found that continuation of this batchwise extraction is desirable until the alcohol extract no longer forms guanidine picrate when treated with alcoholic picric acid. For reasons not clearly understood, detergent-active guanidine petroleum sulfonates do not react with alcoholic picric acid. Ordinarily 3 to 4 extractions using one volume of alcohol per volume of oil per extraction suffices to complete the desired separation. Residual alcohol is stripped from the oil-detergent solution to give a concentrate suitable for direct addition to lubricating oils. The activity or potency of the detergent is determined from its nitrogen content on the basis of a stoichiometric N/S weight ratio of 1.33/1. The sulfonate sulfur content is then computed to arrive at the quantity of active ingredient available. On the basis of equivalent sulfonic acid radicals, our guanidine petroleum sulfonates are equal to or better than conventional calcium and barium sulfonate detergents.

An alternative alcohol extraction procedure may be employed where the viscosity of the unsulfonated oil is too high for use in light lubricants. Thus, extraction may be carried out at moderately elevated temperatures of about 90 to 120° F. until substantially complete removal of sulfonate is realized. The picric acid test, previously referred to, when applied to the extract fractions is a useful first indication of the oil-solubility of product sulfonates. After evaporation of the alcoholic solvent, the semi-solid or plastic guanidine sulfonates are dissolved in a carrier oil of suitable viscosity, the concentration of active ingredient being determined by the nitrogen content as previously described.

Another alternative in the petroleum sulfonate purification procedure results in substantial economy with respect to guanidine carbonate but requires additional investment in corrosion resistant equipment. In this variation the crude sulfonation mixture is washed free of soluble acidic substances with water. The sulfonic acids are then extracted with an alcohol such as isopropanol to yield an oil substantially free of sulfonic acids and an alcoholic mixture of petroleum sulfonic acids containing only a minor proportion of oil. The alcoholic solution is neutralized with aqueous guanidine carbonate and the aqueous phase is separated. The sulfonates are then separated into oil-soluble and substantially oil-insoluble guanidine sulfonates as previously described.

While guanidine itself has been the base used to illustrate the various types of sulfonates of our invention, other derivatives of guanidine such as alkyl or aryl guanidine, halogen substituted guanidine or condensed derivatives of guanidine may be used. With variations in the base it is necessary to use selected fractions of sulfonic acids in order to secure the desired solubility characteristics of the product. Examples of the above types of bases are methyl guanidine, monophenyl guanidine, diphenyl guanidine, wax substituted guanidines, chloroguanidine, phenyl biguanide, ammelide, diorthotolylguanidine, amyl guanidine, and the like. Thus when employing the term "a guanidine salt" herein it is meant to include not only guanidine itself but also substituted guanidines as described above.

The advantages of this invention are illustrated in the following examples. The reactants and their proportions and their specific ingre-

dients are presented as being typical and should not be construed to limit the invention unduly.

EXAMPLE I

Topped Mid-Continent crude was distilled to produce two separate distillates corresponding to SAE 10 and 20 raw base stocks. The final distillation kettle product or vacuum reduced crude was then subjected to a two step solvent extraction employing liquid propane as the selective solvent. The propane extract of the first step contained oil of an average viscosity of about 100 SUS @ 210° F. (SAE 50 base stock) and the propane extract of the second step contained oil of an average viscosity of about 220 SUS @ 210° F. (SAE 250 base stock).

The raw SAE 250 base stock was recovered from the total extract of the second extraction step and then subjected to solvent extraction employing phenol as the selective solvent and to propane solvent dewaxing to produce a highly paraffinic raffinate comprising a lubricating oil stock having the following properties:

Viscosity, SUS @ 100° F. -----	5313
Viscosity, SUS @ 210° F. -----	223.3
Viscosity index -----	89
Gravity, ° API @ 60 F. -----	24
Average molecular weight -----	730

A solution of 1000 grams of the lubricating oil stock described above dissolved in liquid ethylene chloride was slowly mixed with a solution of 176 grams of sulfur trioxide also dissolved in liquid ethylene chloride at a temperature maintained within the limits of 75 to 115° F. at atmospheric pressure, under which conditions reaction of sulfur trioxide with the lubricating oil began almost immediately to produce petroleum sulfonic acid. Reaction was completed shortly after admixing of the reactants was terminated.

To the resulting reaction mixture (including ethylene chloride) was added 103 grams of guanidine carbonate. The mixture was stirred vigorously at a temperature within the limits of 70 to 110° F., whereby the guanidine carbonate reacted with the acidic constituents to produce a mixture of guanidine petroleum sulfonates, guanidine sulfate, guanidine sulfite and traces of guanidine carboxylates. Ethylene chloride was then removed from the reaction mixture by vaporization.

The total reaction product, free of ethylene chloride, comprised guanidine petroleum sulfonates in oil solution and was admixed with an equal volume of anhydrous isopropyl alcohol with vigorous stirring, at a temperature near the boiling point of the alcohol at atmospheric pressure. Under these conditions the guanidine petroleum sulfonate reaction product and oil were dissolved in the alcohol. The alcohol mixture contained some suspended solids and was filtered at its existing temperature. The filtrate was permitted to cool to room temperature, and a large portion of the solute then separated therefrom, as a gummy viscous liquid. The cooled alcohol solution, i. e., at about 70° F., containing guanidine petroleum sulfonates not readily dispersible in oil was decanted from the separated viscous liquid, the latter comprising an oil solution or dispersion of oil-soluble guanidine petroleum sulfonates. The oil solution was then washed with alcohol at room temperature and the washings were added to the previously decanted liquid. The remaining alcohol was stripped from the gummy viscous liquid, and the

liquid was purified, i. e., freed of occluded salts, by dissolving it in benzene, washing the benzene solution with water, and then stripping until the product was benzene-free. The purified product consisted of 600 grams of a dark brown, viscous oil solution of guanidine petroleum sulfonate, and is referred to hereinafter in this example as the "alcohol-insoluble product," i. e., insoluble at room temperature. Several properties of the alcohol-insoluble product are listed as follows:

Specific gravity, 60/60 F. -----	0.8887
Gravity, ° API @ 60 F. -----	27.7
Per cent nitrogen -----	1.08

Alcohol was stripped from the decanted alcohol solution described above. The remaining alcohol-free liquid was purified by dissolving it in toluene, water washing, and then stripping until free of toluene. Toluene was used in the purification of this liquid instead of benzene, in view of its higher boiling point, thus permitting a higher solution purification temperature for the guanidine petroleum sulfonates. The resulting purified guanidine petroleum sulfonates, soluble in isopropyl alcohol at 70° F., as compared with the alcohol-insoluble liquid described above, are referred to hereafter in this example as "alcohol-soluble" guanidine petroleum sulfonate.

The alcohol-soluble and alcohol-insoluble guanidine petroleum sulfonates were each incorporated with separate portions of a lube oil base, and each resulting blend was tested in accordance with the NBS stability test (McKee and Fritz, "Analytical Chemistry" 21, 568, 1949). In carrying out this test, thermal stability of an oil, in this case a lubricating oil containing a guanidine petroleum sulfonate as an additive, is determined by passing it as a thin film over a steel strip under controlled temperature conditions, over a specified period, and the amount of any resulting deposition of degradation product on the strip is measured. Flat steel strips are employed. The tests conducted were modified in two particulars: (1) the steel strips were curved slightly upward at the edges to prevent the test oil from running off the sides, and (2) a single 12 hour period was used instead of the two 6 hour periods. Each product, i. e., the alcohol-soluble and the alcohol-insoluble guanidine petroleum sulfonate, was added to the base oil¹ in a concentration which yielded an oil-additive solution containing the same number of milliequivalents of additive as does a 2 per cent solution of a commercially available detergent sold under the trade name of "Paranox 64" and comprising an alkaline earth metal salt of an alkylphenol sulfide. A blend of the same base oil with 4 volume per cent of Paranox 64 was tested in the same manner for comparison. The results of these thermal stability tests are summarized in the following tabulation:

Material tested	Deposit, mg.	Appearance of strip
Base oil ¹ -----	90.6	Poor.
Base oil + alcohol-soluble guanidine petroleum sulfonate. -----	2.247	Very poor.
Base oil + alcohol-insoluble guanidine petroleum sulfonate. -----	12.6	Very good.
Base oil + 4 percent Paranox 64. -----	9.8	Do.

¹ A solvent refined SAE 30 lubricating oil containing 0.75 volume percent of a commercially available oxidation inhibitor, PzS_2 -related terpenes.

² The alcohol-soluble guanidine petroleum sulfonate did not dissolve completely in the base oil.

The alcohol-insoluble guanidine petroleum sulfonate was evaluated as a lubricating oil additive by dissolving it in the base oil already described and then testing the resulting blend in a mounted single cylinder H2 Lauson test engine operated under conditions simulating the CRC L-4 test conditions. The test performed consists of placing 900 grams of the lubricating oil in the crankcase of the single cylinder engine, and operating the engine under a 1.2 H. P. load at 1600±20 R. P. M., while maintaining a cooling jacket temperature of 210° F., and oil temperature of 310° F., and an air to fuel ratio of 13.5:1. At the end of 60 hours operation under these conditions, the engine is stopped, disassembled, and the piston, crankcase, and bearings are examined. The piston varnish, crankcase, base sludge, overall varnish and carbon, and overall sludge are rated on an arbitrary scale of 1 to 10, the value 10 representing as nearly perfect as ascertainable, number 1 being "very poor" and numbers 2 to 9 each representing intermediate ratings. As a standard for further evaluation of the blend of lubricating oil and alcohol-insoluble guanidine petroleum sulfonate, the same base oil, but without added guanidine petroleum sulfonate, was tested in exactly the same manner. The base oil blend tested contained the same per cent by weight of the alcohol-insoluble guanidine petroleum sulfonate as used in the strip test described in the foregoing paragraph. For a further comparison, a blend of the same base oil with 4.4 volume per cent of a commercially available oil detergent sold as Lubrizol 67 and comprising a barium petroleum sulfonate was tested in the Lauson engine, in the same manner. This latter blend of base oil with Lubrizol 67 contained the same number of equivalents of sulfonate groups as the tested blend containing guanidine petroleum sulfonate. The following is a tabulation of the results of the Lauson type engine test described:

	Base oil ¹	Base oil + alcohol-insoluble guanidine petroleum sulfonate ²	Base oil + alcohol-insoluble guanidine petroleum sulfonate ³	Base oil + 4.4 volume percent Lubrizol 67 ⁴
Piston varnish	5.0	9.0	9.8	9.0
Crankcase and base sludge	6.2	8.2	8.8	8.8
Overall sludge	7.0	8.5	8.9	8.8
Overall varnish and carbon	6.3	8.4	9.3	8.6
Ring sticking	10.0	10.0	10.0	9.0
Bearing weight loss, mg.	12.1	3.8	7.3	4.6

¹ Solvent refined SAE 30 lubricating oil, containing 0.7% volume percent of a commercially available oxidation inhibitor comprising 1,2,3-trimethyl-5-tert-butyl-4-hydroxybenzene.

² This blend contains an amount of Lubrizol 67 in a concentration equivalent to the number of active detergent groups in an oil containing 2 volume percent Paranox.

³ This blend contains an amount of alcohol-insoluble guanidine petroleum sulfonate in a concentration equivalent to the number of active detergent groups in an oil containing 4 volume percent Paranox 64.

⁴ This blend contains an amount of alcohol-insoluble guanidine petroleum sulfonate in a concentration equivalent to the number of active detergent groups in an oil containing 2 volume percent Paranox 64.

The data listed in the preceding tabulation clearly illustrate that the ash-free guanidine petroleum sulfonates of our invention are comparable in effectiveness with well established commercial metal-containing detergents.

EXAMPLE II

A water solution containing guanidine carbo-

nate in slight excess of that required to react with sodium petroleum sulfonate was added with agitation to an aqueous dispersion of a commercially available sodium petroleum sulfonate maintained at 70° F. Under these conditions the sodium petroleum sulfonate reacted with the guanidine carbonate to form a firm plastic mass which separated from the resulting reaction mixture, and which upon cooling formed a gel that while suitable as a grease was not suitable for use as an oil detergent. This reaction demonstrates that a guanidine petroleum sulfonate detergent material of our invention cannot be prepared merely by reacting a commercially available petroleum sulfonic acid or a salt thereof, with a guanidine salt such as guanidine carbonate. Further, it demonstrates the commercially available sodium petroleum sulfonate to be sufficiently water-soluble to be reactive in aqueous medium with guanidine carbonate.

EXAMPLE III

The SAE 250 lube oil stock of Example I was sulfonated in accordance with the procedure of Example I. The petroleum sulfonic acid product was then converted to a sodium salt by neutralization with sodium hydroxide, and the total resulting neutralization product was subjected to solvent extraction with isopropyl alcohol at room temperature. A portion of a resulting alcohol-insoluble sodium salt thus formed, was treated with aqueous guanidine carbonate in accordance with the procedure of Example II. No reaction appeared to take place and the sodium sulfonate layer was separated from the aqueous guanidine carbonate layer and then contacted with a fresh aqueous guanidine carbonate solution. The sulfonate layer was again separated and water washing was attempted but resulted in formation of a stable emulsion. A sample of the sulfonate layer upon analysis for nitrogen was found to contain 0.55 per cent nitrogen. The sulfated ash content of the sulfonate product was determined and was found to be 4.68 per cent, indicating a high sodium content. These two analytical results indicate that the sodium petroleum sulfonate of this example was substantially unreacted with the guanidine carbonate. In this regard the sodium petroleum sulfonate prepared from the SAE 250 oil, as already described in this example, differs markedly from the commercially available petroleum sodium sulfonate of Example II, inasmuch as in the present example the sodium petroleum sulfonate is too insoluble in water to be reacted with the aqueous guanidine carbonate, whereas the commercially available sodium petroleum sulfonate was sufficiently soluble in water so as to be reacted with guanidine carbonate.

EXAMPLE IV

An additional portion of the isopropyl alcohol-insoluble sodium petroleum sulfonate prepared as described in Example III was treated in the same manner as in Example III except that barium chloride was substituted for guanidine carbonate. The resulting reaction product was analyzed for sulfated ash. The sulfated ash formed was leached with water to remove water-soluble ash. The total sulfated ash content was 18.2 per cent and the water-insoluble sulfated ash content was only 1.6, thus indicating that the alcohol-insoluble sodium petroleum sulfonate was substantially unreactive to form the barium salt. These data further distinguish the commercially

15

available sodium petroleum sulfonates from the sodium petroleum sulfonates of Example III inasmuch as that material can be converted to the barium salt by the method of this example.

EXAMPLE V

Listed as oil compositions I-V in the following tabulation are several lube oil blends and also a base oil free of any additive material, each of which was evaluated in a series of Lauson engine tests of the type described in Example I. These evaluation tests are summarized as follows:

	Composition				
	I	II	III	IV	V
Lubricating oil, volume percent.....	100.0	99.25	99.0	94.75	94.50
Oxidation inhibitor, volume percent.....	0.0	0.75	0.5	0.75	1.00
Guanidine octadecyltoluene sulfonate, weight percent.....	0.0	0.0	0.5	0.0	0.0
U. B. Bray detergent, weight percent.....	0.0	0.0	0.0	4.5	4.5

¹ Commercially available (P_{25} -sulfonated terpenes) oxidation inhibitor.

The oil employed as the base oil in these compositions was a solvent-refined Mid-Continent oil of lubricating grade having the following characteristics:

Gravity API	30.3
Viscosity, SUS at 210° F.	61.8
Viscosity index	98
Neutralization No.	0.01

	Rating of composition (evaluation scale, 1-10)				
	I	II	III	IV	V
Piston varnish rating.....	9.2	7.9	8.4	9.8	9.5
Crankcase and base sludge rating.....	9.0	8.6	8.2	8.0	9.3
Overall varnish and carbon rating.....			8.4		
Overall sludge rating.....			8.7		
Bearing weight loss, mg.	1,085	6.5	1.2	201	180

The data of Example V illustrate the base oil alone to exhibit desirable piston varnish ratings and crankcase and base sludge ratings. However use of the base oil alone results in high bearing weight loss. Accordingly an oxidation inhibitor is employed as illustrated in column II for the purpose of reducing bearing weight loss. The use of such an inhibitor effectively reduces piston varnish rating, and crankcase and base sludge rating. Guanidine octadecyltoluene sulfonate, although it contains only 26 carbon atoms in the molecule and is for that reason less desirable than are other oil detergents having a larger number of carbon atoms in the molecule, provides an improvement in the bearing weight loss and in the varnish rating of the base oil tested.

EXAMPLE VI

A guanidine petroleum sulfonate detergent was prepared substantially in accordance with the procedure outlined hereinbefore. The petroleum sulfonation stock was the same as described in Example I. Batch sulfonation was carried out in a stainless steel vessel by slowly adding with agitation 450 grams of SO_3 , stabilized against polymerization, and dissolved in 2000 grams of ethylene chloride, to 4000 grams of oil dissolved in 3000 grams of ethylene chloride. The sulfonation temperature was maintained at 70° F. throughout the reaction. The reaction mixture was immediately neutralized by stirring in 700

16

grams of commercial guanidine carbonate in the form of an aqueous slurry. The neutralized reaction mixture was washed four times with water using one volume of wash water per volume of total reaction mixture per wash. The ethylene chloride solvent was evaporated from the water-washed product and separation of undesirable guanidine sulfonates was effected by multiple batch extraction with isopropyl alcohol. Four batch extractions were carried out using 2 volumes of the alcohol per volume of hydrocarbon phase in the first extraction and $\frac{2}{3}$ volume of alcohol in the subsequent extractions. After evaporation of isopropyl alcohol from the final extraction residue the yield of guanidine petroleum sulfonates plus unreacted oil amounted to 2500 grams. The total nitrogen content of this concentrate was 0.96 per cent by weight which indicates a guanidine petroleum sulfonate content of about 20 per cent by weight.

For purposes of engine evaluation 21.4 weight per cent of the above concentrate was added to a base oil, the same as that of Example I, which contains the oxidation inhibitor primarily to provide bearing protection for the test engine. Expressed as the number of ionic weight equivalents the preceding blend provides a concentration of guanidine and sulfonate groups exactly equal to that of the barium and phenate groups contained in a 4 volume per cent concentration of the commercial detergent "Paranox 64" in the same base oil, also containing 0.75 volume per cent of the oxidation inhibitor. The two test oils, therefore, were exactly equivalent insofar as concentration of surface active groups are concerned; i. e., two sulfonate molecules per one "Paranox 64" molecule since the latter contains 2 active phenolic groups per molecule.

Parallel engine tests were completed on both of the above oils using a modified H2-Lauson engine operating under severe conditions simulating the CRC L-1 diesel engine test for lube oil detergents. The essential test difference between these tests and those of Example I are: oil temperature 225° F. and jacket temperature, 300° F. On completion of the tests, the engines were rated as described in Example I to give the following results:

	Base oil + oil-soluble guanidine petroleum sulfonate	Base oil + 4 volume percent Paranox 64
Piston varnish	7.4	7.7
Crankcase and base sludge	8.5	9.2
Overall sludge.....	8.6	9.2
Overall varnish and carbon.....	7.1	7.1
Oil ring plugging	9.8	9.9
Ring sticking.....	6.7	10.0
Bearing weight loss, mg.	6.3	10.5

¹ The same as employed in Example I.

The above results are especially significant inasmuch as Paranox 64 is a qualified diesel oil detergent capable of passing the stringent L-1 test. The only unfavorable comparison between the two additives is that of ring sticking where the actual difference was not as pronounced as the rating would indicate.

EXAMPLE VII

Table 1 gives the physical properties of the white mineral oil used in the preparation and attempted preparation of greases as shown in Table 2.

Table 2 shows clearly how the alkyl aryl sul-

17

fonates of the metals ordinarily used in grease making did not form the proper gels under similar conditions as did the corresponding sulfonates of guanidine. Listed across the top of the table are the various aromatics and the olefins with which they were alkylated. After alkylation, each alkyl aromatic was sulfonated and then neutralized to form the salt of the element or compound in the left-hand vertical column. In each column beneath the particular alkyl aromatic indicated are the results of attempting to form a grease with the mineral oil described in Table 1.

Table 3 indicates the micropenetration of two of the better greases, those formed with guanidine dodecyltoluene-sulfonate and guanidine hexadecyltoluene sulfonate, shown in Table 2, per indicated strokes of a grease worker. The test method used for determining the micropenetration of the grease is that of the American Society for Testing Materials and is designated as ASTM, D217-47T, as modified according to "Industrial and Engineering Chemistry," analytical edition, vol. 11, pp. 108-110 (1939). The micropenetration is the distance, measured in tenths of a millimeter, which the cone penetrates the grease in 5 seconds. According to this method, an ASTM penetrometer is used with a modified cone weighing 20 grams. The grease of which the penetration is to be measured is put in the grease container holding about 3 to 5 grams and the top surface leveled off. The container is then placed on the penetrometer base and tested. The grease worker referred to above is also described in the indicated ASTM test method. It briefly comprises a cup with a top for closing through which extends a plunger. Attached to the plunger is a perforated plate which, when the grease worker is in operation, passes back and forth forcing the grease in the cup to pass through the perforations.

Table 4 shows the decrease in the micropenetration for the guanidine dodecyltoluene sulfonate grease, for which the micropenetrations per indicated strokes in the grease worker are shown in Table 3, after sitting undisturbed for the times indicated.

TABLE 1

Characteristics of white mineral oil used

Viscosity at 100° F. SUS.	183.2
Viscosity at 210° F. SUS.	44.92
Viscosity index.	90.0
Refractive index, n_D^{20}	1.4748
Specific gravity, D_4^{20}	0.8690
Specific dispersion.	102

18

TABLE 3

Work stability

	Micropenetration at indicated working strokes						
	1	60	1,000	5,000	10,000	20,000	100,000
5 Guanidine dodecyltoluene-sulfonate grease.							
10 Guanidine hexadecyltoluene-sulfonate grease.	45	45	62	82	91	115	177

TABLE 4

Reversion of guanidine dodecyltoluene sulfonate worked 100,000 times

	Total time of sitting undisturbed at room temperature in hours	Micropenetration
20	0.	147
	1.0	71
	3.5	55
	6.0	49
	20.0	43
25	48.0	40

EXAMPLE VIII

This example shows another great advantage of our invention, that of utilizing a mixture of olefins for alkylating the aromatic. In this instance, a fraction of cracked naphtha boiling in the range of 245 to 260° C. and containing only 40 per cent olefins was used to alkylate toluene. This product was sulfonated and then neutralized with guanidine carbonate. The olefins, some of which were branched, had the double bond in various positions in addition to the 1-position. Thus, it is shown that our invention may be practiced successfully using easily obtained refinery cuts without extensive purification.

The grease was made by dispersing 20 parts by weight of the guanidine sulfonate in 80 parts by weight of the mineral oil by heating to a temperature of between 200 and 240° C. and then cooling. The resulting gel was then milled to a smooth grease.

Table 1 gives the physical properties of the mineral oil used to form the grease with the guanidine alkyl aryl sulfonate.

In Table 5 the micropenetration of the grease prepared as described above is compared with that of three commercial all-purpose greases purchased on the open market. Grease A was a barium base grease made from lube oil in which the gelation agent was derived from fatty acids.

TABLE 2

Radical with which salt is formed	Hydrocarbon group				
	Methylbutene-1-benzene	Octene-1-toluene	Decene-1-toluene	Dodecene-1-toluene	Hexadecene-1-toluene
Lithium	Soft plastic mass; slight gel.	Soluble in oil; no gel.	Soluble in oil; no gel.		
Sodium	Insoluble in oil.	Slight gel.			
Potassium		Insoluble in oil; waxy solid.	Soluble in oil; no gel.	Soluble in oil; no gel.	Soluble in oil; no gel.
Calcium	Insoluble in oil; waxy solid.	Soluble in oil; no gel.	do.		
Strontium		do.			
Barium		Very weak gel.	Weak gel.	Soluble in oil; no gel.	Slight gel.
Guanidine	Insoluble in oil; no gel.	Insoluble in oil; no gel.	Fair grease.	Weak gel. Good grease.	Weak gel. Good grease.

19

Great B was a lithium base grease having the gelation agent made by treating fatty acids. Commercial grease C is a sodium base grease of which the gelation agent was made by saponifying nonedible tallow with sodium hydroxide. As may be observed, our grease is equal to or better than the comparative greases. Note that commercial grease B exceeded a penetration of 420, which is about the maximum measuring limit of the penetrometer, after only 10,000 strokes in the grease worker.

TABLE 5

Work stability

	Micropenetration at indicated working strokes							Change in micropenetration between 1,000 and 100,000 strokes	Percent change in micropenetration between 1,000 and 100,000 strokes
	1	60	1,000	5,000	10,000	50,000	100,000		
Guanidine alkyl aryl sulfonate grease.	27	52	79	93	94	122	146	67	85.
Commercial grease A	125	124	145	175	192	244	269	124	86.
Commercial grease B	158	193	275	380	420			Above 145 at 10,000.	Above 52 at 10,000.
Commercial grease C	53	73	107	137	151	199	237	127	119.

EXAMPLE IX

A soft grease was made by using the guanidine salt of an alkyl aryl sulfonic acid in which the olefins used in producing the alkyl aromatic boiled in the range of 190° to 200° C., and the aromatic was toluene. Only a small portion of the thus formed soap or gelation agent dispersed in the mineral oil used; however, the portion which did, produced a satisfactory soft grease.

EXAMPLE X

This example compares in Table 6 the characteristics of our grease with a commercial soda base grease of similar character as tested by the conventional grease testing method CRC designation L-24-745 in a wheel bearing tester, built by Precision Scientific Company and as described in the above reference.

TABLE 6

	Guanidine sulfonate grease worked 100,000 strokes prior to testing	Commercial soda base grease worked 100,000 strokes prior to testing
Flow of grease from:		
(a) Hub	Very slight.	None.
(b) Spindle	None.	Do.
Leakage:		
(a) Wt. in grams	3.0	0.9.
(b) Grease or oil	Grease only.	Grease and oil.
Condition of grease:		
(a) Structure change	None.	Slightly more fibrous.
(b) Micropenetration change	146 to 54.	309 to 61.
Condition of bearing:		
(a) Deposits	None.	None.
(b) Film of lubricant or dry	Lubricated.	Lubricated.

EXAMPLE XI

In this example a white mineral oil, very similar in properties to that used in the previous two examples, was used. This oil was admixed with the sodium, barium, and guanidine salts of trihexyltoluene sulfonic acid under conditions described in this specification hereinabove. It is clearly shown by the data in Table 7 below that the guanidine salt was the only one which made a satisfactory grease. It is also shown that a satisfactory grease may be made by using between 5 and 32 weight per cent of the guanidine salt. The sodium and barium salts used in amounts in about the middle of this range were unsatisfactory. Although a gel was formed in the case of barium, on sitting for several days, it becomes a liquid again.

20

TABLE 7

Radical with which salt is formed	Salt concentration, wt. percent	Results
Sodium	17.5	Soluble, no gel.
Barium	21.0	Gel after cooling, liquefies after several days.
Guanidine	5.0	Soft, clear grease.
Do.	32.1	Hard, brittle waxy cake, mills to stiff grease.

EXAMPLE XII

This example shows in Table 8 the lack of utility of trying to make a suitable grease by attempting to disperse a guanidine salt, of the fatty acids used in grease making as their metal salts, in a mineral oil. A mineral oil similar to those used in the previous examples was used here.

TABLE 8

Salt	Solubility in oil
Guanidine laurate	Insoluble, stratified on cooling.
Guanidine stearate	Hard waxy cake, worked to poor grease.
Phenylbiguanidine cerotate.	Poor grease.

In reiteration, advantages of our invention are the manufacture of a good lubricating grease from products of petroleum, thus eliminating the necessity of using animal and vegetable fatty acids; the production of a substantially ashless grease; the utilization of compounds not ordinarily satisfactory for grease making; and utilization of particular refinery cuts without extensive purification.

As will be evident to those skilled in the art, various modifications can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the claims.

We claim:

1. A method for the manufacture of an oil detergent, comprising sulfonating a deasphalted and solvent-refined petroleum bright stock containing at least 40 carbon atoms in the molecule, neutralizing a resulting sulfonic acid with a guanidine compound selected from the group consisting of guanidine and a basic guanidine salt, resulting neutralization product containing oil-soluble and oil-insoluble guanidine petroleum sulfonates, separating oil-soluble guanidine petroleum sulfonates from oil-insoluble guanidine petroleum sulfonates is said neutralization product, and recovering said oil-soluble guanidine sulfonate as a detergent product of the process.

2. A method for the manufacture of an oil detergent, comprising subjecting a deasphalted and solvent-refined petroleum bright stock having at least 40 carbon atoms in the molecule to sulfonation employing sulfur trioxide as a sul-

fonating agent; neutralizing petroleum sulfonic acids thus formed with a guanidine compound selected from the group consisting of guanidine and a basic guanidine salt; subjecting product of said neutralization to the solvent action of an alcohol containing from 1 to 6 carbon atoms in the molecule, and recovering a portion of said neutralization product insoluble in said alcohol, as a detergent product of the process.

3. A method for the manufacture of an oil detergent, comprising deasphalting a petroleum bright stock having at least 40 carbon atoms in the molecule and a viscosity within the limits of 80 to 600 SUS at 210° F., by propane fractionation; solvent-refining a resulting deasphalted bright stock, and sulfonating a resulting raffinate by dissolving same in a solvent chemically inert to a sulfonation described hereafter, and contacting the resulting solution at a temperature within the limits of 50 to 200° F., with sulfur trioxide dissolved in from 2 to 5 times its weight of anhydrous ethylene chloride, in an amount to provide a sulfur trioxide to petroleum bright stock mol ratio of from 1:1 to 3:1; neutralizing a resulting sulfonation reaction mixture by contacting same with an amount of an aqueous solution of a guanidine compound selected from the group consisting of guanidine and a basic guanidine salt, to provide a resulting neutralization product mixture having a pH of from 6 to 8; removing ethylene chloride and said chemically inert solvent from said neutralization product mixture; contacting a resulting solvent-free neutralization product mixture with an alcohol having from 1 to 6 carbon atoms in the molecule, in a volume ratio of alcohol to said neutralization mixture of from 0.3:1 to 3:1; forming an alcohol-insoluble phase during said contacting, and recovering said alcohol-insoluble phase as a detergent product of the process.

4. The method of claim 3 wherein the last said contacting is conducted at a temperature above 100° F., wherein said mol ratio of sulfur trioxide to bright stock is about 1:1, and wherein subsequent to the last said contacting alcohol is maintained at a temperature below 100° F., and at least a portion of said alcohol-insoluble phase thereby precipitates from said alcohol.

5. The method of claim 3 wherein said inert solvent is ethylene chloride, wherein phenol as a selective solvent is employed in said solvent-refining, and wherein said alcohol is isopropyl alcohol.

6. A method for the manufacture of an oil detergent comprising sulfonating a deasphalted solvent-refined petroleum bright stock having at least 40 carbon atoms in the molecule while employing sulfur trioxide as the sulfonating agent; water washing total sulfonation reaction product formed; alcohol extracting water washed sulfonation reaction product and separating an alcohol phase from the extraction system containing unsulfonated oil and petroleum sulfonic acids; neutralizing petroleum sulfonic acids in said alcohol phase by admixing said alcohol phase with an aqueous solution of a guanidine compound selected from the group consisting of guanidine and a basic guanidine salt; and recovering an oil solution of alcohol-insoluble guanidine petroleum sulfonates from the product of neutralization as a detergent product of the process.

7. The method of claim 6 wherein said alcohol-insoluble guanidine petroleum sulfonates are separated from said oil by alcohol extraction, and

wherein alcohol is vaporized from the extract formed during the last said extraction.

8. The method of claim 3 wherein said raffinate is an SAE 250 base stock prepared by the propane fractionation of a topped crude and the phenol extraction of the resulting deasphalted bright stock.

9. The method of claim 1 wherein said basic guanidine salt is guanidine carbonate.

10. A method for the manufacture of a gelation agent for incorporation with a mineral oil to produce a grease, comprising sulfonating a deasphalted and solvent-refined petroleum lubricating oil stock containing at least 20 carbon atoms in the molecule, neutralizing resulting petroleum sulfonic acids with a guanidine compound selected from the group consisting of guanidine and a basic guanidine salt, resulting neutralization product containing oil-soluble and oil-insoluble guanidine petroleum sulfonates, separating oil-insoluble guanidine petroleum sulfonates from oil-soluble guanidine petroleum sulfonates in said neutralization product, and recovering said oil-insoluble guanidine petroleum sulfonates as gelation agent products of the process.

11. A lubricating oil containing in solution from 0.1 to 25 weight per cent of an oil-soluble guanidine salt, of an organic sulfonic acid, selected from the group consisting of a synthetic alkyl aryl sulfonic acid and a petroleum sulfonic acid.

12. A lubricating oil containing in solution from 0.1 to 25 weight per cent of an oil-soluble guanidine salt of a petroleum sulfonic acid.

13. A composition of claim 12 wherein said petroleum sulfonic acid contains from 40 to 70 carbon atoms in the molecule.

14. A lubricating oil containing in solution from 0.1 to 25 weight per cent of an oil-soluble guanidine salt of a synthetic alkyl aryl sulfonic acid.

15. The composition of claim 14 wherein said alkyl aryl sulfonic acid contains from 24 to 70 carbon atoms in the molecule.

16. A lubricating oil containing in solution from 0.1 to 0.5 weight per cent of guanidine octadecyltoluene sulfonate.

17. A lubricant comprising at least 0.1 weight per cent of a guanidine salt of an organic sulfonic acid selected from the group consisting of a synthetic alkyl aryl sulfonic acid containing at least 10 carbon atoms in the alkyl groups, and a petroleum sulfonic acid containing at least 20 carbon atoms in the molecule, incorporated in a mineral oil.

18. A grease lubricant of claim 17 comprising said mineral oil incorporated with a guanidine salt of a petroleum sulfonic acid containing from 20 to 40 carbon atoms in the molecule.

19. A grease lubricant of claim 17 comprising said mineral oil incorporated with a polyguanidine petroleum sulfonate containing from 20 to 35 carbon atoms per sulfonate group.

20. A lubricant of claim 17 wherein said guanidine salt is a salt of a substituted guanidine.

21. A lubricating oil composition comprising a solvent refined SAE 30 lubricating oil base stock, in solution with an oil soluble guanidine salt of an organic sulfonic acid selected from the group consisting of a synthetic alkyl aryl sulfonic acid and a petroleum sulfonic acid, said composition containing from 0.1 to 25 weight per cent of said oil-soluble guanidine salt.

22. The composition of claim 21 wherein said oil soluble salt is a guanidine salt of a synthetic

alkyl aryl sulfonic acid containing from 24 to 70 carbon atoms in the molecule.

23. The composition of claim 21 wherein said oil-soluble salt is a guanidine salt of a petroleum sulfonic acid containing from 40 to 70 carbon atoms in the molecule.

24. In the oil lubrication of engine parts during operation of an engine, wherein oil deteriorative reactions take place to form oil sludge, and wherein said oil sludge deposits and accumulates on the engine parts to cause general malfunction, the improvement of preventing said deposition and accumulation of sludge, comprising lubricating said engine parts with a lubricating oil containing from 0.1 to 25 weight per cent of an oil-soluble guanidine salt of an organic sulfonic acid selected from the group consisting of a synthetic alkyl aryl sulfonic acid and a petroleum sulfonic acid.

25. The improvement of claim 24 wherein said guanidine petroleum sulfonic acid contains from 40 to 70 carbon atoms in the molecule.

26. The improvement of claim 24 wherein said alkyl aryl sulfonic acid contains from 24 to 70 carbon atoms in the molecule.

27. As a new class of compositions, guanidine petroleum sulfonates containing more than 20 carbon atoms in the molecule.

28. A mineral oil-soluble guanidine petroleum sulfonate derived from a propane fractionated solvent refined petroleum bright stock having a viscosity within the limits of 80 and 700 SUS at 210° F.

29. A guanidine salt of a petroleum sulfonic acid containing from 40 to 70 carbon atoms in the molecule.

30. A guanidine petroleum sulfonate containing more than 20 but not more than 40 carbon atoms in the molecule.

31. A mineral oil-soluble guanidine petroleum sulfonate derived from a propane fractionated solvent refined petroleum bright stock having a viscosity index within the limits of 200 and 230 SUS at 210° F., by first sulfonating said bright stock and then neutralizing the petroleum sulfonic acid thus formed, with guanidine.

32. A diguanidine salt of a petroleum disulfonic acid containing from 70-80 carbon atoms in the molecule.

33. A lubricant containing at least 0.1 weight per cent of guanidine dodecyltoluene sulfonate.

34. A lubricant containing at least 0.1 weight per cent of guanidine hexadecyltoluene sulfonate.

35. A lubricant containing at least 0.1 weight per cent of guanidine trihexyltoluene sulfonate.

36. A lubricant comprising a sufficient quantity of a guanidine alkyl aryl sulfonate containing at least 10 carbon atoms in the alkyl groups dispersed in a mineral oil to cause an increase in the viscosity of the oil.

37. A lubricant comprising 5 to 60 weight per cent of a guanidine alkyl aryl sulfonate containing 10 to 20 carbon atoms in the alkyl groups in mineral oil.

38. A lubricating grease comprising 15 to 50 weight per cent of a guanidine alkyl aryl sulfonate containing a total of 10 to 20 carbon atoms in the alkyl groups dispersed in mineral oil.

39. A lubricant comprising a sufficient quantity of a guanidine alkyl aryl sulfonate dispersed in a mineral oil having a viscosity index above 60 to cause an increase in the viscosity of the oil, wherein the total number of carbon atoms in the alkyl groups of said sulfonate are within the range of 10 to 20.

40. A lubricating grease comprising 5 to 60 weight per cent of a guanidine alkyl aryl sulfonate, wherein the total number of carbon atoms in the alkyl groups is at least 10, dispersed in a mineral oil having a viscosity in the range of 50 to 4000 SUS at 100° F., wherein said sulfonate is prepared by alkylating an aromatic hydrocarbon with olefins boiling in the range of 230 to 250° C., sulfonating the alkylated aromatic hydrocarbon, and forming the guanidine salt of the sulfonate.

41. A lubricating grease comprising 5 to 60 weight per cent of a guanidine alkyl aryl sulfonate dispersed in a mineral oil having a viscosity in the range of 125 to 500 SUS at 100° F., wherein the alkyl groups of said sulfonate contain a total of 10 to 20 carbon atoms per molecule.

42. A lubricating grease comprising 5 to 60 weight per cent of a guanidine alkyl aryl sulfonate, wherein the total number of carbon atoms in the alkyl groups is at least 10, dispersed in a mineral oil having a viscosity in the range of 125 to 500 SUS at 100° F., wherein said sulfonate is prepared by alkylating an aromatic hydrocarbon with olefins boiling in the range of 190 to 315° C., sulfonating the alkylated aromatic hydrocarbon, and forming the guanidine salt thereof.

43. A lubricating grease comprising 15 to 50 weight per cent of a guanidine alkyl aryl sulfonate dispersed in a mineral oil having a viscosity in the range of 50 to 700 SUS at 100° F., wherein the alkyl groups of said sulfonate contain a total of 10 to 20 carbon atoms per molecule.

44. A lubricating grease comprising 15 to 50 weight per cent of a guanidine alkyl aryl sulfonate, wherein the total number of carbon atoms in the alkyl groups is at least 10, dispersed in a mineral oil having a viscosity in the range of 50 to 700 SUS at 100° F., wherein said sulfonate is prepared by alkylating an aromatic hydrocarbon selected from the group consisting of benzene, naphthalene, diphenyl, anthracene, and their lower alkyl homologs with olefins boiling in the range of 190 to 315° C., sulfonating the alkylated aromatic, and forming the guanidine salt thereof.

45. A polyguanidine petroleum polysulfonate containing one sulfonate group per 20 to 35 carbon atoms.

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