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REACTION PRODUCTS OF METAL PETROLEUM SULFONATE, MALEIC ANHYDRIDE AND AN AMINE AS LUBRICANT ADDITIVES

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ABSTRACT OF THE DISCLOSURE

Superior additives for lubricants are provided by a process comprising interreacting a metal petroleum sulfonate, a maleic anhydride, and an amine. Lubricating oil compositions containing said additives are also provided.

This invention relates to improved additives for lubricants. In one aspect this invention relates to methods of preparing said improved additives. In another aspect this invention relates to lubricant compositions containing said improved additives.

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 frequently encountered in the operation of 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.

Metal petroleum sulfonates have been widely used as detergent additives for lubricating oils. Various methods have been employed for the preparation of said metal petroleum sulfonates. Generally speaking, said methods comprise the sulfonation of a petroleum fraction to obtain a mixture of sulfonic acids and unsulfonated oils, and neutralizing the reaction mixture with the carbonate, oxide, or hydroxide of a metal to obtain a mixture of the corresponding metal petroleum sulfonate and unsulfonated oils. The metal petroleum sulfonate can then be recovered from said last-mentioned mixture, if desired. Generally speaking, all metals are suitable for preparing metal petroleum sulfonates. Metals which have been used in such processes include the alkaline earth metals, such as calcium; and other metals, including lead, nickel, cobalt, tin, zinc, etc. Calcium is a presently preferred metal.

Metal petroleum sulfonates, such as calcium petroleum sulfonates, are known which have really good detergent properties in lubricating oil. However, I have now discovered that the detergent properties of metal petroleum sulfonates can be improved by reacting the metal petroleum sulfonate with an anhydride, such as maleic anhydride or an alkyl maleic anhydride, and an amine. Thus, broadly speaking, the present invention resides in the reaction product or products obtained when a metal petroleum sulfonate is reacted with an anhydride and an amine as new additives for lubricating oils, methods of preparing said new additives, and lubricating oil compositions containing said new additives.

An object of this invention is to provide an improved

or superior additive for lubricating oils. Another object of this invention is to provide a process for preparing said improved or superior lubricating oil additive. Another object of this invention is to provide an improved lubricant composition containing said superior lubricating oil additive. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

Thus, according to the invention, there is provided a process for producing a superior additive for lubricants, which process comprises: introducing a metal petroleum sulfonate into a reaction zone; introducing an anhydride selected from the group consisting of maleic anhydride, alkyl substituted maleic anhydrides wherein the alkyl group contains from 1 to 6 carbon atoms, and mixtures thereof into said reaction zone; introducing an amine selected from the group consisting of primary amines containing from 2 to 10 carbon atoms, alkylene polyamines having the formula $H_2N[(CH_2)_xNH]_yH$ wherein x is an integer of from 2 to 6 and y is an integer of from 1 to 100, and mixtures thereof; interreacting said sulfonate, said anhydride, and said amine in said reaction zone; and recovering said additive from the resulting reaction mixture.

Further according to the invention, there is provided, as a new additive for lubricants, a product additive obtained by the process described in the preceding paragraph.

Still further according to the invention, there is provided a new lubricating oil composition, comprising a major proportion of a lubricating oil base stock and a minor proportion, sufficient to impart detergency to said oil, of a new additive in accordance with the invention.

A wide variety of reaction conditions can be employed in the practice of the invention. Any reaction conditions under which the reactions involved in the invention will take place are within the scope of the invention. Similarly, any proportions of reactants which will react with each other to produce a product additive of the invention are within the scope of the invention. However, as will be understood by those skilled in the art in view of this disclosure, certain reaction conditions and reactant proportions are favored for economic reasons, i.e., the reactions proceed faster and give greater yields for some reaction conditions and some proportions of reactants. The reaction or reactions involved in preparing the product additives of the invention can be carried out in the presence or absence of a diluent which is chemically inert, i.e., does not react with the reactants or reaction products.

Generally speaking, in the practice of the invention, said anhydrides are used in an amount within the range of from 0.5 to 10 equivalents of anhydride per equivalent of metal petroleum sulfonate used. Similarly, said amines are used in an amount within the range of from 0.25 to 10 equivalents of amine per equivalent of metal petroleum sulfonate used.

As used herein and in the claims, unless otherwise specified, the term "equivalent" refers to one chemical equivalent weight of a reactant. Thus, for example, one equivalent of maleic anhydride equals 98.02 grams, the chemical equivalent weight and also the molecular weight. One equivalent of citraconic anhydride equals 112.08 grams, the chemical equivalent weight and also the molecular weight. One equivalent of the amines used in the practice of the invention is defined as the amine molecular weight divided by the number of $—NH_2$ groups. The effect of secondary amine groups in the polyamines will be small and for practical purposes can be disregarded. One equivalent of the metal petroleum sulfonates used in the practice of the invention is based on the sulfonate content. Said sulfonate content can be conveniently determined by titrating an aliquot of a chloroform dilution of the metal petroleum sulfonate with a standard solution

of cetyl pyridinium bromide using methylene blue as indicator. While the equivalent weight of the metal petroleum sulfonates will vary with the method of preparation and degree of sulfonation, said equivalent weight will, generally speaking, usually be in the order of 2000 grams.

The interreaction of said metal petroleum sulfonate, said anhydride, and said amine can be carried out at any temperature at which the reactions involved will proceed. Broadly speaking, said interreaction can be carried out at temperatures within the range of from 75 to 500° F., preferably 150 to 450° F. As will be understood by those skilled in the art in view of this disclosure, and as set forth hereinafter, more preferred temperature ranges can be employed when said interreaction of reactants is carried out in one of the several reaction formats which are within the scope of the invention.

A wide range of reaction times can be employed in the practice of the invention. Broadly speaking, the reaction time employed for the interreaction of said reactants will be within the range of from one minute to 50 hours, preferably within the range of from 0.5 to 25 hours. Again, as will be understood by those skilled in the art in view of this disclosure, and as set forth hereinafter, more preferred reaction times can be employed when said interreaction of reactants is carried out in one of the several reaction formats which are within the scope of the invention.

Generally speaking, any metal petroleum sulfonate prepared in accordance with methods known in the art can be used as a starting reagent in the practice of the invention. Methods disclosed in U.S. 3,135,693, issued June 2, 1964, to W. B. Whitney et al., are exemplary of methods which can be used in preparing metal petroleum sulfonates which can be used in the practice of this invention.

A wide variety of oils can be used as the charge oil in preparing the metal petroleum sulfonates used in the practice of the invention. Preferably, said charge oil is selected from more viscous bright stock fractions of petroleum. A petroleum fraction having a viscosity of at least 90 SUS at 210° F. will produce a metal petroleum sulfonate which is satisfactory 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. A presently more preferred sulfonation charge stock is a propane fractionated, solvent extracted, and dewaxed Mid-Continent oil of about 200 to about 230 SUS at 210° F. and having a viscosity index of about 85 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 petroleums 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 feedstock. The raffinate from the solvent extraction step is then dewaxed.

Sulfonating agents which are known to the art can be utilized in the sulfonation step in preparing said metal petroleum sulfonates. Sulfonating agents which can be so used include fuming sulfuric acid and liquid SO_3. Said fuming sulfuric acid can vary from 10 weight percent to 40 weight percent excess SO_3. However, when sulfuric acid is used it is usually preferred to use commercial fuming sulfuric acid which contains about 20 weight percent excess SO_3. Liquid SO_3, i.e., liquid SO_3 in liquid SO_2, is the presently preferred sulfonating agent for use in preparing the metal petroleum sulfonates used in the practice of the invention. Such liquid SO_3 is commercially available.

When 20 percent fuming sulfuric acid is used as the sulfonating agent, the acid-oil ratio can be in the range of from about 0.1:1 to about 0.7:1, or even 1:1 to produce the metal petroleum sulfonates used in the practice of the invention. A preferred range of acid-oil ratios is in the range of about 0.3 to about 0.6:1. When liquid SO_3 in liquid SO_2 is the sulfonation agent, the SO_3 to oil weight ratios are maintained equivalent to those available from the 20 percent fuming sulfuric acid values given above. In other words, the SO_3 to oil ratio can be in the range of about 0.02 to 0.2, preferably about 0.06 to about 0.12:1. Said SO_3 to oil ratios can be controlled by varying the rate of flow of the oil or of the SO_3-containing medium, or both. The above given ratios are weight ratios.

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 may take place. A reaction time of about 20 to about 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, usually less than about five minutes.

The sulfonation reaction can be carried out at atmospheric pressure although pressures greater or less than atmospheric also can be employed, if desired. When using liquid SO_3 in liquid SO_2 as the sulfonating agent, it is preferred to carry out the reaction at sufficient pressure to maintain the SO_2 in liquid phase.

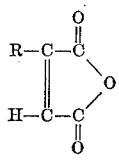
The neutralization of the acid oil obtained in the sulfonation step can be carried out in any suitable manner. One satisfactory method comprises contacting said acid oil with the chosen neutralizing agent in any suitable mixing vessel employing conventional mixing means, at a temperature above about 100° F., for a period of time sufficient to effect the neutralization, and recovering a mixture of metal petroleum sulfonate and unsulfonated oil.

If desired, the metal petroleum sulfonates can be separated from the residual unsulfonated oil associated therewith by means of extraction with propane and/or butanes under appropriate conditions of temperature and pressure. 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 about 150 to about 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 about 290 and about 305° F. The conditions required when isobutane is required are intermediate those for propane and for normal butane.

Further details regarding the preparation of metal

petroleum sulfonates which can be used in the practice of the invention will be known to those skilled in the art; for example, see said Whitney et al. patent.

Anhydrides which can be used in the practice of the invention include maleic anhydride and alkyl-substituted maleic anhydrides wherein the alkyl group contains from 1 to 6 carbon atoms and can be cyclic or acyclic. Such anhydrides can be represented by the formula



wherein R is selected from the group consisting of a hydrogen atom, and alkyl and cycloalkyl groups containing from 1 to 6 carbon atoms. Examples of said anhydrides include, among others, the following: maleic anhydride, methyl maleic anhydride (citraconic anhydride), ethyl maleic anhydride, butyl maleic anhydride, cyclobutyl maleic anhydride, hexyl maleic anhydride, cyclohexyl maleic anhydride, and the like.

A wide variety of amines can be used in the practice of the invention. Presently preferred amines for use in the practice of the invention include (a) those containing from 2 to 12 carbon atoms per molecule and represented by the formula RNH_2 wherein R is alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkylcycloalkyl, cycloalkylalkyl, cycloalkylaryl, or arylcycloalkyl and (b) those polyamines represented by the formula

$$H_2N[(CH_2)_xNH]_yH$$

wherein x is a whole integer of from 2 to 6, inclusive, and y is a whole integer of from 1 to 10, inclusive. Examples of suitable amines which can be used in the practice of the invention include, among others, the following: ethylamine, butylamine, 3-methylcyclopentylamine, decylamine, dodecylamine, cyclohexylamine, aniline, naphthylamine, 3,5-diethylcyclohexylamine, m-toluidine, 2,3 - xylidine, benzylamine, 3-cyclohexylbutylamine, 4-cyclohexylaniline, 4 - phenylcyclohexylamine, 3-methyl-4-phenylcyclopentylamine, ethylene diamine and its homologues, diethylene triamine, triethylene tetramine, tetraethylene pentamine, dipropylene triamine, butylene diamine, hexamethylenediamine, tetrahexenepentamine, heptabutyleneoctamine, decapenteneundacamine, and the like.

The improved additives of the invention can be prepared by interreacting the above-described reactants, i.e., metal petroleum sulfonate, anhydride, and amine in a number of different ways. To some extent the actual reaction conditions employed will depend upon the specific reaction procedure employed. Thus, while the above-described general reaction conditions are applicable in the practice of the invention, more precise reaction conditions are sometimes preferred and employed in specific reaction procedures. For example, in one method of preparing the additives of the invention, a metal petroleum sulfonate, an anhydride, and an amine are charged to and reacted substantially simultaneously in a reaction zone. When the reactants are interreacted in this manner, it is preferred that the mixture of reactants be refluxed at a temperature within the range of from 150 to 350° F., more preferably 175 to 250° F., for a period of time within the range of from about 0.5 to 24, more preferably 1 to 5 hours, in the presence of a chemically inert diluent. Preferably, said diluent is one capable of forming an azeotrope with water. This provides one convenient method of removing the water formed during the reaction since during said refluxing a diluent-water azeotrope can be removed. Said diluent is then removed, as by distillation, and the remaining reaction mixture is maintained at a temperature within the range of from 250 to 500° F., preferably 375 to 450° F., for a period of time within the range of from 0.25 to 50 hours, preferably 0.5 to 25 hours. The product additive can then be recovered from the reaction mixture in any suitable manner, as described hereinafter.

I have discovered that there are at least two principal reactions involved in preparing the additives of the invention, (1) a reaction between the metal petroleum sulfonate anhydride, and (2) a reaction between said metal petroleum sulfonate anhydride and the amine. It has been established by infrared analysis that the product of reaction (2) contains a succinimide structure. Thus, for convenience, said product is referred to herein as a metal petroleum sulfonate imide. I have also discovered that said reaction (1) proceeds slower than said reaction (2). Thus, in one presently preferred manner of practicing the invention, it is preferred to carry out said reaction (1) to substantial completion and then carry out said reaction (2). Thus, in one presently more preferred method for preparing the additives of the invention, a mixture of the metal petroleum sulfonate and the anhydride is heated to a temperature within the range of from 300 to 500° F., preferably 375 to 450° F., for a period of time within the range of from one minute to 50 hours, preferably within the range of 0.5 to 4 hours. After cooling the resulting reaction mixture, the amine is added thereto and the temperature maintained within the range of 75 to 500° F., preferably 150 to 350° F., for a period of time within the range of from 0.25 to 25 hours, preferably 0.5 to 2 hours. The product additive can then be recovered from the reaction mixture in any suitable manner, as described hereinafter.

In another presently less preferred method of preparing the additive of the invention, a mixture of a metal petroleum sulfonate and an anhydride is heated at a temperature in the range of 300 to 500° F., preferably 375 to 450° F., for a period of time within the range of from one minute to 50 hours, preferably within the range of from 1 to 4 hours, to form a metal petroleum sulfonate anhydride as an intermediate reaction product. The resulting reaction mixture is then cooled, a chemically inert diluent such as toluene is added, and the mixture is then filtered. Diluent and other volatile material are removed from the filtrate by distillation at reduced pressure. The intermediate reaction product remaining from said distillation is then dissolved in another portion of inert diluent, the resulting solution warmed, and the amine added thereto for reaction with said intermediate reaction product to form a metal petroleum sulfonate imide. The product additive can then be recovered from the resulting reaction mixture in any suitable manner as described hereinafter.

Several different methods of recovering the product additive from the reaction mixture can be employed. The particular additive recovery method employed will depend to some extent on the method of interreacting the metal petroleum sulfonate, the anhydride, and the amine. It is desirable that essentially all the water formed during the reaction or reactions, or which is otherwise present, be removed. This can be done in any suitable manner. One method is to add to the reaction mixture a chemically inert diluent which is capable of forming an azeotrope with water, and then refluxing the diluted reaction mixture under azeotropic distillation conditions to remove a diluent-water azeotrope. After the water has been removed, the remaining diluent is removed from the reaction mixture by distillation, preferably vacuum distillation. If desired, said diluent can be employed as a diluent or solvent for one or more of the reactants and can be present in the reaction zone during the reaction or reactions. Thus, said diluent can be added along with one of the reactants or a reactant can be dissolved in the diluent and the resulting solution added to the other reactant or reactants. Any diluent which is chemically inert, i.e., does not react chemically with the metal petroleum sulfonate, the anhydride, the amine, or the reaction prod-

uct can be used in the practice of the invention. Presently preferred diluents are the hydrocarbons containing from 5 to 12 carbon atoms per molecule. Examples of suitable diluents include, among others, the following: normal pentane, normal hexane, normal decane, normal dodecane, benzene, toluene, the xylenes, cyclohexane, alkyl-substituted cyclohexanes, and the like. Said diluents are normally employed in diluent to reaction mixture ratios within the range of from 1:1 to 1:5.

If desired, the water can be removed from the reaction mixture by blowing the heated reaction mixture, e.g., at a temperature within the range of from 350 to 500° F. for a period of time within the range of from 0.5 to 2 hours, with an inert gas such as nitrogen, helium, argon, crypton, neon, xenon, or mixtures thereof.

It is also preferred that any insoluble finely divided solids be removed from the reaction product. Materials of this nature are sometimes formed in side reactions. Such materials can be removed by diluting the reaction mixture with one of the above-described diluents and then filtering through a suitable filter medium. Also, since such materials in most instances are low molecular weight materials, they can be removed by stripping the heated reaction mixture with an inert gas. Said filtration can be carried out in conjunction with and/or prior to the water removal, if desired. For example, the diluent can be added to the reaction mixture, the resulting dispersion filtered and the water removed from the filtrate, as by azeotropic distillation.

If desired, the product additive of the invention can be recovered as a solution or other dispersion in a light lubricating oil such as an SAE 10 lube oil base stock or blending stock. In such instances said lubricating oil is preferably added to the reaction mixture after the water and diluent have been removed. However, if desired, said lubricating oil stock can be added to the reaction mixture prior to removal of said diluent therefrom.

In another and sometimes more preferred method for recovering the product additive of the invention, the reaction mixture can be extracted with a suitable solvent to concentrate the calcium petroleum sulfonate imide and any unreacted calcium petroleum sulfonate associated therewith. The solvent extraction step is preferably carried out after removal of water and/or diluent from the reaction mixture. Any suitable solvent can be employed. Examples of suitable solvents are, for example, methyl isopropyl ketone, methyl ethyl ketone, methyl isobutyl ketone, and like ketones having at least four carbon atoms and preferably 4 to 8 carbon atoms per molecule. Said solvents will generally be employed in a solvent to oil ratio within the range of from 2:1 to 20:1. Said solvent extraction step can be carried out by adding the solvent to the reaction mixture in any suitable manner, and heating to a sufficient temperature, such as in the range of 200 to 225° F., to dissolve the reaction mixture in the solvent. After solution or dispersion is complete, the solution is cooled and the resulting two immiscible layers are separated. The metal petroleum sulfonate imide and unreacted metal petroleum sulfonate will be concentrated in the raffinate phase. Solvent can be recovered from the raffinate phase and the extract phase in conventional manner. The solvent-free raffinate comprises a concentrated or oil-free additive of the invention.

The above-described product additives of the invention comprise a metal petroleum sulfonate imide. As indicated above, depending upon the metal petroleum sulfonate used and its method of preparation and also upon the method of recovering the metal petroleum sulfonate imide, other materials can be associated with said metal petroleum sulfonate imide in the product additives of the invention. For example, metal petroleum sulfonates commonly have some unsulfonated oil associated therewith, the amount depending upon the extent to which the metal petroleum sulfonate has been concentrated. Any unsulfonated oil associated with the starting metal petroleum sulfonate reactant will remain largely unreacted except for possibly a small amount which may react with the anhydride. Similarly, metal petroleum sulfonate which remains unreacted with the anhydride and/or the amine, and any metal petroleum sulfonate anhydride which remains unreacted with the amine, can also be associated with the metal petroleum sulfonate imide in the product additives of the invention.

I have also discovered that the alkaline reserve of the above-described additives comprising a metal petroleum sulfonate imide can be increased by contacting same with a calcium-containing material produced by passing carbon dioxide through a mixture comprising methanol and lime (CaO and/or $Ca(OH)_2$), either by adding the previously produced calcium material to said additive, or by producing the calcium material in the presence of said additive. One presently preferred method comprises bubbling carbon dioxide through a mixture comprising (a) said additive, (b) lime (CaO and/or $Ca(OH)_2$), and (c) methanol. Said lime will usually be present in an amount, based on equivalent calcium oxide, within the range of from 2 to 70 parts by weight per 100 parts by weight of said additive. Said methanol will usually be present in an amount within the range of from 10 to 150 parts by weight per 100 parts by weight of said additive. The amount of carbon dioxide used will usually be within the range of from 0.5 to 5 parts by weight per 1 part by weight of calcium compound present. If desired, a chemically inert hydrocarbon diluent such as naphtha or one of the above-described hydrocarbon diluents can also be present in said mixture. Said diluent can be employed in any convenient amount, e.g., 100 to 400 parts by weight per 100 parts by weight of said additive.

The product additives of this invention can be incorporated into lubricating oil compositions in several combinations depending upon specific service requirements. For example, if desired, in the case of heavy duty oils, such as those used in trucks, buses, and general diesel applications the oil-free or concentrated additive of the invention can be blended with suitable lubricating oil base stocks. In many general duty crankcase oils, the unconcentrated product additive of the invention can be blended with appropriate base oils. In these variations of blending, the additives of the invention will provide high quality lubricating oils as required in various ordnance and other qualification tests and other specifications, and outstanding performance with respect to sludge formation in stop-and-go engine operation.

Generally speaking, the product additives of the invention comprising a metal petroleum sulfonate imide can be added to the base lubricating oil in an amount sufficient to obtain the desired degree of improvement characteristics of the base oil. Said product additives can be added to said base oil in amounts of about 0.2 to about 30 weight percent of the finished oil. The concentration of metal petroleum sulfonate imide alone in the base oil is normally in the range of about 0.1 to about 15 weight percent of the finished oil and a presently preferred concentration of said product additive comprising metal petroleum sulfonate imide and unsulfonated oil is in the range of about 2 to 20 weight percent of the finished oil. A presently preferred concentration of metal petroleum sulfonate imide in the finished oil is in the range of about 1 to about 10 weight percent of the finished oil.

The following examples will serve to further illustrate the invention.

Example I

A calcium petroleum sulfonate was prepared from a solvent refined, dewaxed lubricating oil fraction derived from a Mid-Continent petroleum, and having the following properties: Viscosity of 4272 SUS at 100° F., viscosity of 212.4 SUS at 210° F., and viscosity index of 96.9. The charge stock, identified as finished 250 stocks, was sulfonated with a 10 percent SO_3-90 percent SO_2 mixture

in a continuous operation. The SO_3 to oil weight ratio was 0.07 to 0.08 and the temperature of the reaction was controlled at about 115° F. The total reaction time was about 5 minutes, including the mixing and soaking periods. The system was maintained in liquid phase at a pressure of 100–120 p.s.i.g. Effluent from the sulfonation unit was subjected to a two-stage flash for SO_3-SO_2 removal. The resulting acid oil was then neutralized with a mixture of lime, water, and Stoddard solvent in a now conventional manner, the neutralized mixture stabilized, and solvent and water removed therefrom, all substantially as described in Example I of said Whitney et al. patent except that the water-free, solvent-free calcium petroleum sulfonate product was not propane extracted. The resulting calcium petroleum sulfonate had the following properties: Sulfonate, 0.5 meq./gram; TBN, 7.8; ash, 4.7 wt. percent; and SUS @ 210° F., 1547.

A mixture of 100 grams of the above-described calcium petroleum sulfonate, 4.9 grams of maleic anhydride, and 35 ml. of toluene were heated to 135° F., with stirring, and then cooled to 110° F. A solution of 3.8 ml. of diethylenetriamine in 20 ml. toluene was added dropwise during a 9-minute period. The resulting mixture was then refluxed under azetropic distillation conditions for 1 hour to remove a water-toluene azeotrope and thus remove water from said reaction mixture. The toluene was then removed by distillation and the remaining mixture heated to 400° F., and maintained at that temperature for 21 hours. After cooling to 200° F., 160 ml. of toluene was added and the resulting solution or dispersion filtered through diatomaceous earth. The filtrate was concentrated to about 225 ml. and 50 grams of an SAE 10 lubricating oil base or blending stock was added thereto. The resulting solution or dispersion was then further concentrated by distilling at 370° F. and 10 mm. Hg for one hour. The resulting product additive contained 33 weight percent SAE 10 base or blending stock and had the following properties: oxygen, 2.5 wt. percent; nitrogen, 0.8 wt. percent; sulfur, 1.1 wt. percent; TBN, 8.4; and ash, 2.58 wt. percent.

A carbon spot dispersancy test was carried out on the above product additive blended at a 4 percent concentration in a commercial SAE 10 lubricating oil base stock. The results of said tests showed the product additive possessed excellent detergent properties. In said carbon black dispersancy test, 50 milligrams of carbon black is stirred into 10 grams of an oil blend containing the candidate additive. A drop of the resulting slurry is then dropped onto a polished bronze block heated to a temperature of 500° F. The extent to which the carbon black is carried to the extremity of the resulting oil ring is a measure of the dispersancy or detergent properties of the candidate additive.

Example II

A mixture of 2000 grams of calcium petroleum sulfonate prepared as described in Example I and 116 grams of maleic anhydride was heated to 425° F. and stirred at that temperature, under a blanket of natural gas, for 1 hour. The mixture was then cooled to 250° F. and 45 ml. of diethylene triamine was added dropwise, with rapid stirring, over a period of 13 minutes. The temperature increased to 278° F. during the addition of said amine. The resulting mixture was maintained at 250° F. for 1 hour, cooled to 150° F., diluted with 2000 ml. cyclohexane, and filtered through diatomaceous earth. The filtrate was then vacuum distilled at 395° F. and 10 mm. Hg pressure for 1 hour. The distilland was cooled to 300° F. and 248 grams of a SAE 10 lubricating oil base or blending stock added thereto to produce a product additive containing 11 wt. percent of said base stock, and having the following properties: TBN, 2.4; and ash, 3.75 wt. percent.

Example III

A mixture of 1125 grams (0.56 equivalent) of the calcium petroleum sulfonate prepared in Example I and 65 grams (0.66 equivalent) of maleic anhydride was heated under an atmosphere of natural gas for 21 hours at a temperature within the range of from 380° to 400° F. The resulting mixture was then cooled to 160° F., dissolved in toluene, filtered through diatomaceous earth, and heated to a final temperature of 390° F. at 10 mm. mercury pressure for 1 hour to remove volatile material. A portion (948 grams) of the resulting intermediate product was dissolved in 1500 ml. of toluene, warmed to 100° F., and a solution of 36.5 grams (0.7 equivalent) of diethylenetriamine in 120 ml. of toluene was added over a 45-minute period. Stirring was continued, and the mixture was refluxed under azeotropic distillation conditions to distill off a water-toluene azeotrope. After all the water was removed, 996 grams of an SAE 10 lubricating oil base stock was added and the resulting mixture was heated to a final temperature of 370° F. at 10 mm. mercury pressure for 1 hour to remove volatile material. The resulting product additive contained 50 percent SAE 10 lubricating oil blending stock and 50 percent of reaction mixture.

Said product additive of this Example III and the product additive of the above Example II were compared with the calcium petroleum sulfonate starting material as a control in a low temperature deposition test (Federal Standards 791a, Tentative Method 348–T) using the following lubricating oil blends:

	Parts by weight		
	Ex. II	Ex. III	Control
Calcium petroleum sulfonate			12.5
Product additive of invention	12.5	12.5	
SAE 10 and SAE 50 stocks [1]	79.0	79.0	79.0
Other additives (same in all blends)	8.5	8.5	8.5

[1] Lube oil blending stocks, amounts adjusted to give the same viscosity for all blends; there were about 73 parts of the SAE 10 stock and about 6 parts of the SAE 50 stock. The viscosity of all blends was about 65 SUS at 210° F.

Results of these tests were:

	Ex. II	Ex. III	Control
Piston varnish (10=clean)	9.0	8.7	7.8
Total varnish (50=clean)	47.7	47.0	44.1
Total sludge (50=clean)	43.3	45.6	39.1
Oil ring plugging, percent	0	0	40
Oil screen plugging, percent	0	0	5

It is apparent that the product additives of the invention are considerably better detergents than the calcium petroleum sulfonate starting material.

Example IV

A calcium petroleum sulfonate was prepared from a solvent refined, dewaxed lubricating oil fraction essentially like that used in Example I and having a SUS viscosity at 100° F. of 4029, a SUS viscosity at 210° F. of 205.9, and a viscosity index of 97.3. Said lubricating oil fraction was sulfonated and the calcium petroleum sulonate product recovered in essentially the same manner as described in Example I.

A mixture of 16.46 pounds of said calcium petroleum sulfonate and 426 grams of maleic anhydride was stirred, under nitrogen, heated to 430° F., and kept at that temperature for 1 hour. Unreacted maleic anhydride was removed from the resulting mixture by blowing same with nitrogen for 1 hour at 430° F. An SAE 10 lubricating oil base stock was then added in an amount of 5.80 pounds. The mixture was cooled to 250° F. and 55 ml. of diethylenetriamine added thereto over a period of 5 minutes. Stirring was continued for 5 minutes after addition of the amine was complete. The amine addition was repeated with two more additions of 55 ml. of diethylenetriamine, after which the reaction mixture was maintained at 250° F. for 1 hour. Further blowing with nitrogen at 250° F. yielded no volatile material. The resulting product additive contained 25 percent of the SAE 10 lubricating oil base

stock and had the following properties: TBN, 13.4; nitrogen, 0.61 wt. percent; and sulfur, 1.28 wt. percent.

A stirred mixture of 5.88 pounds of said product additive, 18.5 pounds of naphtha, 500 ml. of methanol, and 400 grams of $Ca(OH)_2$ was bubbled with 60.2 liters of CO_2. The methanol was then stripped out by heating the mixture to 275° F. A portion of the mixture was filtered and then vacuum stripped at 400° F. and 10 mm. Hg pressure to remove the naphtha. The base number of the overbased product additive was 88.5.

Rust rating tests were run on the above-described product additive and overbased product additive. The test procedure used was a modification of ASTM D665–60, Procedure A. In said modification, 30 ml. of 1 percent acetic acid was used instead of 30 ml. of distilled water, and stirring of the oil-acid mixture was for 16 hours instead of 24 hours. Results of the tests were:

Rust Rating (10=clean or perfect)

Product additive	2
Overbased product additive	8

The above tests show that the effective reserve alkalinity of the calcuim petroleum sulfonate imide product additive can be increased by overbasing.

Example V

This example illustrates concentration of the product additive by solvent extraction. Twenty ml. of the product additive of Example II was mixed well with 80 ml. of methyl isobutyl ketone (MIBK) and the mixture then allowed to settle for 30 minutes. The methyl isobutyl ketone or extract layer was withdrawn and stripped of solvent. The raffinate layer was also stripped. Infrared values and ash values were determined on the original product additive, the solvent-free extract, and the solvent-free raffinate. Results were as follows:

	Original product additive	MIBK soluble fraction (extract)	MIBK insoluble fraction (raffinate)
Charge wt., grams	17.8		
Recovered from MIBK, grams		13.15	4.54
Meq of imide/gram	0.40	0.32	0.88
Sulfated ash, wt. percent	3.74	2.51	7.71

This example clearly shows that the MIBK (methyl isobutyl ketone) concentrates the calcium petroleum sulfonate imide and the calcium petroleum sulfonate components in the raffinate fraction.

Example VI

A sample of the overbased product additive of Example IV was extracted with methyl isobutyl ketone solvent in the same manner as set forth in Example V above. The results were as follows:

	Original overbased product additive	MIBK soluble fraction (extract)	MIBK insoluble fraction (raffinate)
Charge wt., grams	18.5		
Recovered from MIBK, grams		13.4	4.78
Meq of imide/gram	0.077	0.051	0.25
Sulfated ash, wt. percent	11.58	5.34	24.55
TBN (total base number)	78.6	43.8	200.6

This example demonstrates that MIBK concentrates the calcium petroleum sulfonate imide and the overbased calcium petroleum sulfonate components into the raffinate.

Total base number values (TBN) were determined in accordance with a modification of ASTM D664–58. In this modified test 2 grams of the product additive are dissolved in 100 milliliters of a 50/50 mixture of benzene and isopropyl alcohol containing 0.5 volume percent water. The mixture is shaken well and the pH determined using a standard pH meter. If the pH of the said mixture is above 4, the mixture is then titrated to a pH of 4 using standard 0.1 N HCl. From this titration TBN, or total base number, is calculated as follows:

$$TBN=\frac{(V)(N)(56.1)}{W}$$

where V=ml. of HCl, N=normality of HCl, and

W=grams

of sample. TBN is reported as mg. of KOH per gram of oil.

While certain embodiments of the invention have been described for illustrative purposes, the invention obviously is not limited thereto. Various other modifications will be apparent to those skilled in the art in view of this disclosure. Such modifications are within the spirit and scope of the invention.

I claim:

1. A process for producing a superior additive for lubricants, which process comprises: introducing a metal petroleum sulfonate into a reaction zone; introducing an anhydride selected from the group consisting of maleic anhydride, alkyl-substituted maleic anhydrides wherein the alkyl group contains from 1 to 6 carbon atoms, and mixtures thereof into said reaction zone; introducing an amine selected from the group consisting of primary monoamines containing from 2 to 10 carbon atoms, alkylene polyamines having the formula $H_2N[(CH_2)_xNH]_yH$ wherein x is an integer of from 2 to 6 and y is an integer of from 1 to 100, and mixtures thereof; interreacting said sulfonate, said anhydride, and said amine in said reaction zone at a temperature of from about 75° F. to about 500° F.; and recovering said additive from the resulting reaction mixture.

2. A process according to claim 1 wherein: said anhydride is introduced into said reaction zone in an amount within the range of from 0.5 to 10 equivalents of anhydride per equivalent of said sulfonate; said amine is introduced into said reaction zone in an amount within the range of from 0.25 to 10 equivalents of amine per equivalent of said sulfonate; and said reactants are interreacted at a temperature within the range of from 75 to 500° F. for a period of time within the range of from 1 minute to 50 hours.

3. A process according to claim 2 wherein: said sulfonate and said anhydride are introduced into said reaction zone and reacted at a temperature within the range of from 300 to 500° F. for a period of time within the range of from 1 minute to 50 hours to produce an intermediate reaction product; and said amine is then added to said reaction zone and reacted with said intermediate reaction product at a temperature within the range of from 75 to 500° F. for a period of time within the range of from 0.25 to 25 hours.

4. A process according to claim 3 wherein: said metal petroleum sulfonate is calcium petroleum sulfonate; said anhydride is maleic anhydride; said amine is diethylenetriamine; said sulfonate and said anhydride are reacted at a temperature within the range of from 375 to 450° F. for a period of time within the range of from 0.5 to 4 hours to form said intermediate reaction product; and said amine is reacted with said intermediate reaction product at a temperature within the range of from 150 to 350° F. for a period of time within the range of from 0.5 to 2 hours.

5. A process according to claim 3 wherein said additive is recovered by solvent extracting the final resulting reaction mixture with an aliphatic ketone containing from 4 to 8 carbon atoms per molecule to form an extract phase and a raffinate phase, and said additive is recovered from said raffinate phase.

6. A process according to claim 2 wherein: said metal petroleum sulfonate is calcium petroleum sulfonate, said anhydride is maleic anhydride, and said amine is diethylenetriamine; said sulfonate, said anhydride, said amine, and a chemically inert diluent are introduced into said reaction zone; the resulting mixture is heated and maintained under reflux and azeotrope distillation conditions

for a period of time at least sufficient to remove water from said mixture by distilling therefrom a water-diluent azeotrope; the remaining diluent is removed by distillation; and the remaining mixture is maintained at a temperature within the range of 250 to 500° F. for a period of time within the range of from 0.25 to 50 hours.

7. A process according to claim 2 wherein: said metal petroleum sulfonate is calcium petroleum sulfonate, said anhydride is maleic anhydride, and said amine is diethylenetriamine; said sulfonate and said anhydride are introduced into said reaction zone and reacted at a temperature within the range of from 300 to 500° F. for a period of time within the range of from 1 minute to 50 hours to form an intermediate reaction product in a first reaction mixture; said intermediate reaction product is recovered from said first reaction mixture; and said amine is reacted with said recovered intermediate reaction product in the presence of a chemically inert diluent at a temperature within the range of from 75 to 500° F. for a period of time within the range of from 0.25 to 25 hours.

8. A process according to claim 4 comprising in further combination: increasing the alkaline reserve of said recovered additive by contacting carbon dioxide through a mixture comprising (a) said additive, (b) a compound selected from the group consisting of calcium oxide and calcium hydroxide in an amount based on equivalent calcium oxide within the range of from 2 to 70 parts by weight per 100 parts by weight of said additive, and (c) from 10 to 150 parts by weight of methanol per 100 parts by weight of said additive; and recovering said thus further treated additive.

9. A lubricant additive obtained by the process of claim 1.

10. A lubricant additive obtained by the process of claim 8.

11. A lubricating oil composition comprising a petroleum lubricating oil base stock containing from about 2 to about 20 weight percent of an additive obtained by the process of claim 4.

12. A lubricating oil composition comprising a petroleum lubricating oil base stock containing from about 2 to about 20 weight percent of an additive obtained by the process of claim 8.

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