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LUBRICANTS CONTAINING REACTION PRODUCTS OF PETROLEUM SULFONIC ACIDS AND ORGANIC NITROGEN POLYMERS

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No Drawing. Original application Dec. 3, 1968, Ser. No. 780,887, now abandoned. Divided and this application Apr. 30, 1971, Ser. No. 139,176
Int. Cl. C10m 1/40, 3/34
U.S. Cl. 252—33 10 Claims

ABSTRACT OF THE DISCLOSURE

Superior additives for lubricants are provided by a process comprising reacting a petroleum sulfonic acid with a polymer of a polymerizable heterocyclic nitrogen base, e.g., a vinylpyridine, and/or a polymer, of 2 1,2-alkylene imine. Lubricating oil compositions containing said additives are also provided.

This application is a division of our copending application Ser. No. 780,887, filed Dec. 3, 1968, abandoned in favor of a continuation-in-part application having Ser. No. 164,092, filed July 19, 1971, now U.S. Pat. 3,766,150, issued Oct. 16, 1973.

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 improved 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, adidtives of this nature are termed "detergents," although it is now understood that they have little utility in cleainng a dirty engine but by virtue of dispersant activity prevent or greatly retard engine fouling.

As cleanliness requirements have called for greater concentrations of detergent additive, the problem of ash deposition in the combustion chamber has become more serious. Especially is this a problem in certain engines which tend to develop violent preignition troubles in the presence of metal-containing ash. These problems have increased the importance and desirability of using "ashless" detergents.

An "ashless" detergent is one which shows substantially no ash when tested by ASTM procedure D-482-59T. The only possible source of metal when using such an additive is that of corrosion products and trace quantities present in some crude oils. It can be generally stated that metal-containing deposits in an engine (1) contribute to valve burning, (2) contribute to preignition, (3) tend to foul and short-out spark plugs and (4) tend to increase octane requirements. Use of conventional metal-containing detergents can contribute to the deposit of metal-containing materials in the combustion chamber. Metal-containing deposits do not form from ashless detergents. Use of an ashless detergent, therefore, materially reduces the problems normally encountered in internal combustion engines in connection with metal-containing deposits.

We have discovered that superior ashless detergents having superior detergent and corrosion inhibiting properties can be prepared by reacting a petroleum sulfonic acid with a polymer of a polymerizable heterocyclic nitrogen base, e.g., a vinylpyridine, and/or a polymer of a 1,2-alkylene imine. Thus, broadly speaking, the present invention resides in the reaction product or products, obtained when a petroleum sulfonic acid is recated with a polymer of a polymerizable heterocyclic nitrogen base and/or a polymer of a 1,2-alkylene imine, as new additives for lubricants; methods of preparing said new additives; and lubricant compositions containing said new additives.

An object of this invention is to provide an ashless additive for lubricants. Another object of this invention is to provide a method for the preparation of an ashless additive for lubricating oils. Another object of this invention is to provide an improved lubricating composition utilizing the ashless additive of the invention. Another object of this invention is to provide a method for the preparation of an improved lubricating oil composition, possessing excellent detergent properties, utilizing the ashless additive of the invention. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art upon studying this disclosure.

Thus, according to the invention, there is provided a process for producing a superior additive for lubricants, which process comprises: introducing a petroleum sulfonic acid reactant into a reaction zone; introducing into said reaction zone a polymer reactant selected from the group consisting of (a) a polymer of a polymerizable heterocyclic nitrogen base, (b) a polymer of a 1,2-alkylene imine, and (c) mixtures of said polymers (a) and (b); and reacting said petroleum sulfonic acid and said polymer reactant to form said additive.

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 polymer reactant and said petroleum sulfonic acid reactant are preferably reacted in a weight ratio of polymer reactant to sulfonic acid in the range of from 0.01:1 to 5:1, more preferably from 0.05:1 to 1:1. However, it is within the scope of the invention to employ operable ratios of polymer to sulfonic acid outside said ranges.

The reaction of said polymer and said petroleum sulfonic acid can be carried out at any temperature at which the reaction(s) involved will proceed. Generally speak-

ing, said reaction is preferably carried out at temperatures within the range of from 75 to 400° F., more preferably 100 to 300° F. However, it is within the scope of the invention to employ operable temperatures outside said ranges.

A wide range of reaction times can be employed in the practice of the invention. Generally speaking, the reaction times employed for the reaction of said reactants preferably will be within the range of from 0.05 to 10 hours, more preferably within the range of from 0.25 to 5 hours. However, it is within the scope of the invention to employ operable reaction times outside said ranges.

Generally speaking, any petroleum sulfonic acid 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 petroleum sulfonic acids 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 petroleum sulfonic acids 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 petroleum sulfonic acid which is satisfactory in many instances. 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. It is preferred that the sulfonation charge stock have 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.

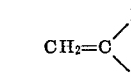
Sulfonating agents which are known to the art can be utilized in the sulfonation step in preparing said petroleum sulfonic acids. Sulfonating agents which can be so used include fuming sulfuric acid and liquid SO_3. Said fuming sulfuric acid can vary from 10 weight percent to 40 weight percent excess 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 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 petroleum sulfonic acids 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 wtih the sulfur trioxide, usually less than about five minutes.

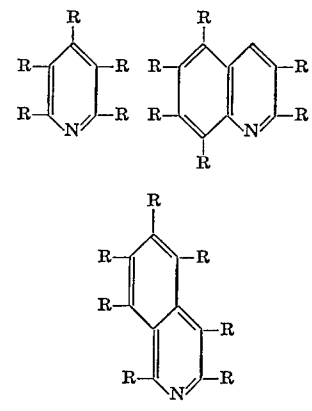
The sulfonation reaction can be carried out at atmospheric pressure although pressures greater or less than atmospheric also can be employed, if desired. When using liquid SO_3 in liquid SO_2 as the sulfonating agent, it is preferred to carry out the reaction at sufficient pressure to maintain the SO_2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

A wide variety of polymers of polymerizable heterocyclic nitrogen bases can be used in the practice of the invention. The polymerizable heterocyclic nitrogen bases which are applicable for the production of polymers used in the practice of the invention are those of the pyridine and quinoline series which contain one and only one



substituent wherein R' is either hydrogen or a methyl group. That is, the substituent is either a vinyl or an alpha-methylvinyl (isopropenyl) group. Of these compounds, the pyridine derivatives are of the greatest interest commercially at present. Various substituted derivatives are also applicable but the total number of carbon atoms in the nuclear substituted groups, such as alkyl groups, should not be greater than 12 because the polymerization rate decreases somewhat with increasing size of the alkyl group. Compounds where the alkyl substituents are methyl and/or ethyl are available commercially.

These heterocyclic nitrogen bases have the formula



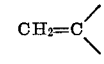
where R is selected from the group consisting of hydrogen, alkyl, vinyl, alphamethylvinyl, aryl, and combinations of these groups such as alkylaryl, and the like; one and only one of said groups being selected from the group consisting of vinyl and alpha-methylvinyl; and the total number of carbon atoms in the nuclear substituted groups being not greater than 12. Examples of such compounds are 2-vinylpyridine; 2-vinyl-5-ethylpyridine; 2-methyl-5-vinylpyridine; 4-vinylpyridine; 2,3,4-trimethyl - 5 - vinyl-

pyridine; 3,4,5,6-tetramethyl - 2 - vinylpyridine; 3-ethyl-5-vinylpyridine; 2,6-diethyl-4-vinylpyridine; 2-isopropyl-4-nonyl-5-vinylpyridine; 2 - methyl - 5 - undecyl-3-vinylpyridine; 2,4-dimethyl-5,6-dipentyl-3-vinylpyridine; 2-decyl-5-(alpha-methylvinyl)pyridine; 2-vinyl-3-methyl-5-ethylpyridine; 3-vinyl-5-phenylpyridine; 2-(para-methylphenyl)-3-vinyl-4-methylpyridine; 2-vinylquinoline; 2-vinyl-4-ethylquinoline; 3-vinyl - 6,7 - di-n-propylquinoline; 2-methyl-4-nonyl-6-vinylquinoline; 4 - (alpha-methylvinyl)-8-dodecylquinoline; 3-vinylisoquinoline; 1,6-dimethyl - 3 - vinylisoquinoline; 2-vinyl-4-benzylquinoline; and the like.

As used herein and in the claims, unless otherwise specified, the term "polymer of a polymerizable heterocyclic nitrogen base" or the term "polymer of a substituted polymerizable heterocyclic nitrogen base" includes homopolymers of said nitrogen bases, copolymers of one or more of said nitrogen bases with another said nitrogen base, and copolymers of one or more of said nitrogen bases copolymerized with another monomer or monomers copolymerizable therewith.

Included among the monomers which can be copolymerized with said nitrogen bases to form copolymers are the conjugated dienes containing from 4 to 8 carbon atoms per molecule such as 1,3-butadiene, isoprene (2-methyl - 1,3 - butadiene), piperylene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, chloroprene, and others. However, in a broader aspect of the invention, conjugated dienes having more than eight, such as twelve, carbon atoms per molecule can be used, particularly where the presence of various isomeric compounds can be tolerated. Furthermore, various alkoxy, such as methoxy and ethoxy, and cyano derivatives of these conjugated dienes, are also applicable. Thus, dienes, such as phenylbutadiene, 2,3-dimethyl-1,3-hexadiene, 2-methoxy-3-ethyl butadiene, 2-ethoxy-3-ethyl-1,3-hexadiene, 2-cyano-1,3-butadiene, and 2,3-diethyl-1,3-octadiene are applicable.

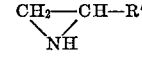
Other monomers which can be copolymerized with said nitrogen bases to form copolymers include those containing an active



group such as aryl olefins, esters of acrylic and substituted acrylic acids, nitriles, amides, ketones, ethers, and halides. Specific examples of such copolymerizable monomers include styrene, various alkyl and substituted alkyl styrenes, 3-phenyl - 3 - butene-1-ol, p-chlorostyrene, p-methoxystyrene, alphamethylstyrene, vinylnaphthalene, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, methyl ethacrylate, acrylonitrile, methacrylonitrile, methacrylamide, methyl isopropenyl ketone, methyl vinyl ketone, methyl vinyl ether, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl furane, vinylcarbazole, vinylacetylene, and the like.

The above-described polymers, including copolymers of said nitrogen bases can be prepared by any of the many methods known to those skilled in the art such as emulsion polymerization, mass polymerization, suspension polymerization, and solution polymerization, employing recipes known in the art. These methods are all known to persons skilled in the art and no further description thereof is believed necessary. For example, further details concerning the preparation of said polymers and said copolymers can be found in U.S. Pat. 3,035,006, issued May 15, 1962, to R. S. Hanner et al. Preferably, said polymers and copolymers are oil soluble, e.g., soluble in lubricating oils and in the diluents which can be used in the reaction zone in the practice of the invention. More preferably, said polymers and copolymers used in the practice of the invention will have an inherent viscosity within the range of from 0.05 to 5, preferably 0.2 to 2, deciliters per gram in a solution containing 0.1 gram of polymer in 100 ml. of pyridine at 30° C.

Polymerized 1,2-alkylene imines which can be used in the practice of the invention include those derived from 1,2-alkylene imines having the formula



in which R'' is H or an alkyl radical. Said polymerized 1,2-alkylene imines can be represented by the empirical formula

$$(C_2H_4R''N)_n$$

wherein n has a value in the range of from 5 to 2000, preferably 10–50. The polymerized 1,2-alkylene imines are preferably polymerization products of ethylene imine and/or propylene imine, although polymerization products derived from higher C-alkyl ethylene imines in which R'' contains up to 14, or more, carbon atoms per molecule, such as 1,2-butylene imine, C-propyl ethylene imine, C-tetradecyl ethylene imine and others are also suitable. The polymerized alkylene imines can be prepared according to methods known in the art. One method comprises treating the corresponding monomers with small quantities of acid catalysts such as hydrochloric acid. Another method comprises condensation of alkylene dichlorides with ammonia. Still another method comprises thermal decarboxylation of 2-oxazolidones. The resultant products contain either branched-chain or straight-chain molecules. Although polymerized 1,2-alkylene imines of essentially any degree of polymerization (n value) may be used, it is preferred that the polyalkylene imines be oil soluble, e.g., soluble in lubricating oils and soluble in the diluents which can be used in the reaction zone. The above-described polyalkylene imines having n values in the range of 5 to 2000 are oil soluble. Polyalkylene imines are available commercially as 40–70% aqueous solutions. One such product is Badische Aniline und Soda Fabrik's "Polymin P," which is a 50% to 70% aqueous solution of polyethylene imine. Another is "Polymin P" (A) which contains about 47% by weight of polyethylene imines, about 53% by weight water, and 4.76 milligram atoms of basic nitrogen per gram. Polyalkylene imines are also available commercially in essentially anhydrous form. For example, three such products are available from Dow Chemical Co. as Montrek 6, Montrek 12, and Montrek 18. These materials are polyethylene imines containing a minimum of 99 weight percent C_2H_5N and having molecular weights of approximately 600, 1200, and 1800, respectively. The essentially anhydrous materials are presently preferred.

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 reacting the petroleum sulfonic acid and polymer reactants. It is desirable that essentially all of any water which may have been added with the reactants or formed during the reaction or reactions 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 petroleum sulfonic acid, the polymer, or the reaction product 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. Small amounts of other materials such as alcohols (methanol, ethanol, and the like) or ketones (acetone, methyl ethyl ketone, and the like) can also be present.

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, krypton, 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 can sometimes be formed in side reactions. Such materials can be removed by diluting the reaction mixture, if necessary, 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 method for recovering the product additive of the invention, the reaction mixture can be extracted with a suitable solvent to concentrate the petroleum sulfonic acid addition product. 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 include, for example, methyl isopropyl ketone, methyl ethyl ketone, methyl isobutyl ketone, and like ketones having at least 4 carbon atoms and preferably 4 to 8 carbon atoms per molecule, phenol, and others. 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 any suitable temperature, such as in the range of from room temperature 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 petroleum sulfonic acid addition product 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 product additive of this invention are oil soluble and can be incorporated into lubricating oil compositions in several combinations depending upon specific 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 petroleum sulfonic acid addition product can be added to the base lubricating oil in an amount sufficient to obtain the desired degree of improvement characteristics of the base oil, e.g., a small but effective amount sufficient to impart increased detergency and/or corrosion resistance of said 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 petroleum sulfonic acid addition product alone in the base oil is broadly in the range of about 0.1 to about 15 weight percent of the finished oil. A presently preferred concentration of said product additive comprising petroleum sulfonic acid addition product and unsulfonated oil is in the range of about 0.5 to 20 weight percent of the finished oil. A presently preferred concentration of petroleum sulfonic acid addition product 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 petroleum sulfonic acid was prepared from a solvent-refined, dewaxed lubricating oil fraction derived from Mid-Continent petroleum and having the following properties: viscosity of about 4200 SUS at 100° C. and about 210 SUS at 210° F., and viscosity index of about 97. This oil, identified as finished 250 stock, was sulfonated with a 10 percent SO_3-90 percent SO_2 mixture in a continuous operation substantially like that described in said Whitney et al. patent. The SO_3 to oil weight ratio was about 0.08 and the temperature of the reaction was controlled at about 115° F. The total reaction time was about 5 minutes, including 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.

EXAMPLE II

A poly(2-methyl-5-vinylpyridine) was prepared using the following recipe:

Azo-*bis*-isobutyronitrile	g	0.25
Water	ml	20
Methanol	ml	30
2-Methyl-5-vinylpyridine	g	20

After charging the reactants the reactor was flushed with nitrogen, and nitrogen was added to a pressure of 5 to 10 p.s.i.g. Reaction was carried out for 7 hours at 158° F., the reaction mixture was dumped into an excess of water, and the polymer was separated, chopped, and dried. Polymer yield was 18.6 g. and the inherent viscosity in pyridine at 30° C. was about 0.6 deciliter per gram.

EXAMPLE III

A mixture of 25 g. of the petroleum sulfonic acid of Example I, 2.4 g. of the polymer of Example II, and 100 ml. of toluene was stirred for 1 hour at room temperature and 1.5 hours at 140–150° F. The solution was filtered and cooled, and 25 grams of a SAE 10 lubricating oil base stock was added thereto. The resulting solution was vacuum stripped at 5–10 mm. Hg and about 300° F. to remove volatile materials and yield a concentrate containing about 50 weight percent reaction product.

EXAMPLE IV

Rust rating tests were run on the above-described invention additive and a commercial calcium petroleum sulfonate additive. In these tests said invention additive (reaction product) and said commercial additive were each tested at 4 weight percent concentration in a SAE 10 lubricating oil stock. The test procedure employed 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:

	Rating [1]
Reaction product of invention	6
Calcium petroleum sulfonate	4

[1] 10=perfect.

EXAMPLE V

A carbon spot dispersancy test was carried out on the above invention additive (reaction product of Example III) blended at a 2 weight percent concentration (½ the normal concentration for the test) in a commercial SAE 10 lubricating oil base stock. The results of said test showed the invention 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 VI

A mixture of 50 grams of the petroleum sulfonic acid of Example I, 250 ml. benzene, and 3.3 grams of Montrek 6 (a commercial anhydrous polyethylene imine having a molecular weight of about 600, available from Dow Chemical Co.) in 10 ml. methanol was refluxed 1 hour. The volatile materials were vacuum-stripped from the reaction mixture at about 300° F. and 5–10 mm. Hg. The resulting product gave an excellent carbon spot dispersancy test when tested as described above in Example V. The results of rust rating tests, run as described in Example IV were: 5½ for said product additive; compared to about 4 for commercial calcium petroleum sulfonate; and 3½ for Monsanto 778 (a commercial alkenylsuccinimide dispersant).

EXAMPLE VII

One thousand grams of a petroleum sulfonic acid essentially like that of Example I, 3000 ml. of toluene, and 50.2 grams of Ionac PP 2040X (a commercial 50–50 copolymer of 2-vinylpyridine and 2-methyl-5-vinylpyridine having an inherent viscosity of 0.87 determined in pyridine at 30° C.) were stirred for 1 hour at room temperature (a 5° F. temperature rise was observed). The mixture was then heated to 175° F., maintained there for 2 hours, 25 grams of said copolymer was added, and stirring continued for 1 hour. The reaction mixture was then filtered, using Celite filter aid. The filtrate was then added to commercial SAE 10 lubricating oil stock and volatiles were vacuum stripped to 300° F. at 5 mm. Hg to yield a concentrate containing 48.8 weight percent lube oil and 51.2 percent reaction product.

The results of a carbon spot dispersancy test carried out as described in Example V showed the invention additive (reaction product) to have excellent detergent properties.

EXAMPLE VIII

A lubricating oil blend having the following composition was prepared:

	Volume percent
SAE 10 base stock	71.6
SAE 50 base stock	9.7
Commercial calcium petroleum sulfonate	8.0
Lubrizol 1395 (zinc dialkyldithiophosphate)	0.7
Acryloid 909 (nitrogen-containing polymethacrylate)	5.5
Invention additive of Example VII	4.4

Said blend was tested in accordance with the Caterpillar I–H test (MIL–L–2104B). The results of this test were as follows:

Top groove carbon	11 percent
First land	trace LAL [1]
Second groove	trace LAL [1]

[1] LAL=Light amber lacquer.

Another lubricating oil blend like that above except that the invention additive of Example VIII was omitted was also tested in accordance with said Caterpillar I–H test. The results of the test were as follows:

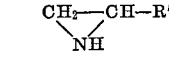
	Percent
Top groove carbon	26
First land (LAL [1])	9
Second groove (LAL [1])	8

[1] LAL=Light amber lacquer.

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

We claim:

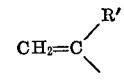
1. A lubricating oil composition comprising a major proportion of a lubricating oil containing a small but effective amount, sufficient to impart increased detergency to said lubricating oil, of an additive which is a reaction product formed by reacting a petroleum sulfonic acid reactant and a polymer reactant selected from the group consisting of (a) a polymer of an ethylenically substituted heterocyclic nitrogen base, (b) a polymer of a 1,2-alkylene imine characterized by the formula



wherein R'' is hydrogen or an alkyl radical containing up to 14 carbon atoms, and having a degree of polymerization within the range of 5 to 2,000, and (c) mixtures of said polymers (a) and (b), said reacting being carried out under reaction conditions and at reactant ratios such that said reaction product is formed.

2. A composition according to claim **1** wherein said lubricating oil contains from about 0.2 to about 30 weight percent of said additive.

3. A composition according to claim **1** wherein said polymer reactant (a) is a polymer of a



substituted heterocyclic nitrogen base selected from the group consisting of pyridine, quinoline, alkyl-substituted pyridine, and alkyl-substituted quinoline, wherein the total number of carbon atoms in the nuclear alkyl substituents is not more than 12 and wherein R' is selected from the group consisting of hydrogen and a methyl radical, said polymer having an inherent viscosity within the range of from about 0.05 to 5 deciliters per gram.

4. A composition according to claim **3** wherein said lubricating oil contains from about 0.2 to about 30 weight percent of said additive.

5. A composition according to claim **1** wherein: said polymer reactant and said petroleum sulfonic acid reactant are introduced into a reaction zone in a weight ratio of polymer reactant to sulfonic acid in the range of 0.01:1 to 5:1; and said reactants are reacted at a temperature within the range of from about 75 to about 400° F. for a period of time within the range of from about 0.05 to 10 hours.

6. A composition according to claim **5** wherein: said reactants are reacted in the presence of a chemically inert diluent at a temperature within the range of about 100 to

about 300° F. for a period of time within the range of about 0.25 to about 5 hours.

7. A composition according to claim 5 wherein; said petroleum sulfonic acid is prepared by sulfonating a petroleum hydrocarbon fraction having a viscosity within the range of 90 to 720 SUS at 210° F. and a viscosity index of at least about 85; and said polymer reactant is a homopolymer of 2-methyl-5-vinylpyridine.

8. A composition according to claim 5 wherein; said petroleum sulfonic acid is prepared by sulfonating a petroleum hydrocarbon fraction having a viscosity within the range of 90 to 720 SUS at 210° F. and a viscosity index of at least about 85; and said polymer reactant is a copolymer of 2-methyl-5-vinylpyridine and 2-vinylpyridine.

9. A composition according to claim 5 wherein: said petroleum sulfonic acid is prepared by sulfonating a petroleum hydrocarbon fraction having a viscosity within

the range of 90 to 720 SUS at 210° F. and a viscosity index of at least about 85; and said polymer reactant is a polyethylene imine.

10. A composition according to claim 9 wherein said polyethylene imine has a molecular weight of about 600.

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252—47.5, 391

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,846,316

DATED : November 5, 1974

INVENTOR(S) : Sidney Schiff and Gerald R. Kahle

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 26, "100°C" should be "100°F"

Signed and Sealed this

second Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks