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DETERGENT LUBRICATING COMPOSITION

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This invention relates to compositions comprising hydrocarbon oil and non-metallic salts of sulfonic acids. More particularly the invention relates to mineral lubricating oils containing hydrocarbon substituted guanidine and biguanide salts of petroleum sulfonic acids.

It is well known that ordinary mineral lubricating oil will not operate satisfactorily in internal combustion engines where conditions of operation are such as to cause sludging of the oil with formation of resinous and varnish-like deposits on engine parts such as piston rings and the like and cause deterioration or corrosion of corrosion-sensitive bearings. These effects are noted in gasoline engines of the automotive type, in diesel engines and particularly in the newer supercharged diesel engines. It has been the practice to add various types of compounds to mineral lubricating oil to prevent deterioration of the oil, sludging, formation of engine deposits and corrosion. However, many of the compounds which have been used in the past to prevent these objectionable features of ordinary lubricating oils lead to other difficulties. For example, metal salts of fatty acids, substituted fatty acids, sulfonic acids and the like have been added to mineral lubricating oil to prevent sludging and prevent formation of varnish and lacquer-like deposits on engine parts. These metal salts are well known in the art as detergents since the prevention of sludging and formation of engine deposits has been considered to be due to the detergent action of the added metal salts. Although the metal salts mentioned appear to impart detergent characteristics to lubricating oils when used in sufficient quantity, the metal content of the oil due to the presence of such metal salts is sometimes increased to an undesirably high degree so that burning of the oil, which occurs on upper cylinder walls and within the combustion chamber, leaves metallic deposits in the form of oxides, sulfates, and the like which are objectionable. Such deposits impair efficient operation of spark plugs in automotive engines and particularly the efficient operation of valves. Thus it has been realized that a highly desirable detergent would be one which has the ability to prevent sludging, formation of lacquer-like engine deposits, and the like, and yet one which does not contain metal as a part of its composition. Such a non-metal detergent material will be referred to herein as an ashless detergent.

It has now been found that non-metal or ashless compounds capable of imparting detergency as well as other desirable characteristics to mineral lubricating oil may be prepared by reacting sulfonic acids with a hydrocarbon substituted guanidine or a hydrocarbon substituted biguanide. The resulting substituted guanidine or biguanide sulfonates are found to impart a high degree of detergency to mineral lubricating oils and to improve to some degree at least the anti-corrosion characteristics of the oil. Moreover, these sulfonates are sufficiently oil-soluble to be useful as detergents and they do not impart any observable undesirable characteristics to lubricating oils.

Thus, it is an object of this invention to produce mineral lubricating oils having good detergency and yet not containing metal salts.

Another object is to produce mineral lubricating oils having high detergency and anti-corrosion characteristics and yet being free from metal salts or containing relatively small amounts of metal in the form of salts.

It is a more particular object of this invention to produce mineral lubricating oils containing relatively small amounts, sufficient to impart detergency to such mineral oils, of hydrocarbon substituted guanidine and/or biguanide salts of oil-soluble petroleum sulfonic acids.

A further object is to produce a detergent, anti-corrosive lubricating oil containing the mentioned substituted guanidine and biguanide sulfonates together with particular anti-corrosion agents which cooperate with the sulfonates to impart such desirable characteristics to the oil.

In preparing the lubricating oils of this invention containing the ashless detergents, oil-soluble petroleum sulfonic acids or their metal salts are converted into the guanidine or biguanide salts which latter non-metal salts are dissolved in lubricating oils. The terms "guanidine" and "biguanide" are used herein in their generic sense to include the various hydrocarbon substituted guanidines and biguanides unless otherwise specifically indicated.

In preparing the guanidine or biguanide salts, oil-soluble petroleum sulfonic acids may be neutralized directly with a guanidine or biguanide compound and the resulting salt added directly to mineral lubricating oil. These non-metal salts may also be produced by metathesis using an alkali metal sulfonate, as for example, sodium sulfonate or potassium sulfonate and the hydrochloride or carbonate of the guanidine or biguanide compound. In such case the products of reaction are the non-metallic sulfonate corresponding to the guanidine or biguanide compound employed and alkali metal chloride or carbonate. The chloride or carbonate may then be removed from the reaction mixture by extraction with water. More specific directions for carrying out the preparation of these non-metallic salts are given in the specific examples set forth hereinbelow.

Lubricating oils which may be employed in the preparation of the detergent lubricating oils of this invention include substantially all types of mineral lubricating oil. The detergent effect is observed in both the naphthenic-type oils, i. e., those having viscosity indices ranging from about 10 to about 65 or 70 as well as in the paraffinic-type lubricating oil having viscosity indices above about 70. Particularly good results have been obtained with a solvent-treated paraffinic-type oil having a viscosity index of about 90. The effect is similarly observed in paraffinic-type oils having viscosity indices of over 100 such as 105.

The guanidine and biguanide compounds which may be employed in the preparation of the corresponding sulfonate salts include the guanidines and biguanides having 1 to 3 hydrocarbon substituents and preferably 1 or 2 hydrocarbon substituents in which the hydrocarbon substituents are selected from the group consisting of alkyl, cycloalkyl, alkylated cycloalkyl, aryl, aralkyl and alkaryl radicals. It is not necessary that all of the substituent groups be the same type of hydrocarbon radical. Thus, one substituent may be aryl, and another alkyl, or one may be aryl and another cycloalkyl, for example. The preferred hydrocarbon substituent, however, is the aryl substituent. Compounds which may be used in preparing the non-metal sulfonates include mono-, di- and triphenyl guanidine, mono-, di- and tri-tolyl guanidine, mono-, di- and tri-benzyl guanidine, mono-, di- and trihexyl guanidine, mono-, di- and tri-lauryl guanidine, mono-, di- and tri-oleyl guanidine, mono-, di- and tricyclohexyl guanidine, mono-, di- and tri-methylcyclohexyl

guanidine, mono-, di- and tri-phenyl biguanide, mono-, di- and tri-tolyl biguanide, mono-, di- and tri-benzyl biguanide, mono-, di- and tri-hexyl biguanide, mono-, di- and tri-lauryl biguanide, mono-, di- and tri-oleyl biguanide, mono-, di- and tri-cyclohexyl biguanide, mono-, di- and tri-methylcyclohexyl biguanide.

The number of carbon atoms in each hydrocarbon substituent present in the guanidine or biguanide compounds may vary from about 2 to 20 or more. Generally each hydrocarbon substituent will preferably contain between about 4 and about 18 carbon atoms. The total carbon atom content of all substituents will preferably be between about 4 and about 40 carbon atoms. If the carbon atom content is above about 40 the resulting sulfonate generally does not impart to the mineral lubricating oil the desired degree of detergency. On the other hand where the carbon atom content of hydrocarbon substituents of the guanidine or biguanide compounds is below about 4 the resulting sulfonates may not be sufficiently soluble in mineral lubricating oil to produce the desirable oils of this invention.

The various hydrocarbon substituted guanidines and biguanides may be prepared by methods well known in the art. Some of these compounds are commercially available. General methods of preparation, however, will be indicated. The aromatic substituted biguanide salts, or aryl biguanide salts, may be prepared by reacting dicyandiamide with an aromatic amine and an equivalent amount of a mineral acid in water at temperatures between about 75° C. and 100° C. Alkyl and cycloalkyl biguanide salts are prepared by reacting alkyl or cycloalkyl amines with dicyandiamide in the presence of an equivalent amount of copper sulfate and treating the resulting complex copper salt with hydrogen sulfide to give the alkyl biguanide sulfate.

The various alkyl, cycloalkyl and alkylated cycloalkyl guanidine salts may be prepared by reacting dicyandiamide with aliphatic, cycloaliphatic and alkylated cycloaliphatic amine salts at temperatures of about 180° C. for about 3 hours. The aryl guanidines such as phenyl and diphenyl guanidine are commercially available and others of this class are obtained by reacting guanidine with the desired aryl amine. This method is applicable to the preparation of all of the various hydrocarbon substituted guanidines described herein.

Generally any oil-soluble petroleum sulfonic acid or its alkali metal salt may be employed in the preparation of the substituted guanidine and biguanide detergents of this invention. Thus the ordinary sodium sulfonate salts of commerce, such as those obtained as a by-product in the production of white mineral oils, which salts have an average molecular weight in the range of about 400 to about 500 are found to produce desirable oil-soluble salts with the guanidine and biguanide compounds disclosed herein. However, improved solubility and improved detergent properties are obtained by using the so-called high molecular weight sulfonate salts of commerce having molecular weights in the range of 450 to 550 and outstanding results have been obtained using sulfonic acids or their alkali metal salts which have been prepared by sulfonating bright stocks or other high viscosity mineral oil fractions such as those having viscosities between about 130–250 seconds Saybolt Universal at 210° F. Viscosity indices of the sulfonation stocks may vary from as low as 35 to 40 to a high as 100 or more. Preferably the viscosity index of the fraction will be between about 50 and about 100.

Suitable sulfonation stocks which may be used in the preparation of sulfonic acids which are to be converted to the guanidine or biguanide salts as described herein include mineral oil fractions having viscosities between 50 and 250 seconds Saybolt Universal at 210° F. Included are the typical stocks used in the commercial preparation of oil-soluble sulfonic acids, i. e., stocks having viscosities of 50 to 65 seconds as well as those of higher viscosity which appear to give sulfonic acids of even more desirable characteristics. Particularly desirable sulfonic acids are obtained by sulfonating petroleum fractions having viscosities in the range of 100 to as high as 250 seconds Saybolt Universal at 210° F. Particularly preferred sulfonation stocks are fractions of petroleum referred to in the industry as "bright stocks" having viscosities of between about 140 and 225 seconds Saybolt Universal at 210° F.

The preferred sulfonic acids will therefore be those acids whose sodium salts have average molecular weights of at least about 450, the corresponding acids having average molecular weights of at least about 428. Of these higher molecular weight sulfonic acids or salts those produced from bright stocks as indicated above are particularly preferred.

In preparing sulfonic acids, the usual methods of sulfonation may be employed such as those used in the preparation of white mineral oils wherein sulfonic acids are a by-product of the process as well as those used in the commercial production of oil concentrates of mahogany sulfonic acids. In the latter case the mineral oil is treated with concentrated or fuming sulfuric acid, or with some other sulfonating agent such as chlorosulfonic acid or the like to effect sulfonation of at least a part of the oil and the sulfonic acids produced by this treatment are separated from unsulfonated oil or not depending upon the ultimate use of the sulfonic acids. Generally the sulfonated oil is neutralized with an alkali hydroxide such as sodium hydroxide and the sodium sulfonates subsequently are converted into the desired sulfonate. In the present use, the sodium sulfonates are converted into the desired guanidine or biguanide salts as described herein. Methods of sulfonation are well known and need not therefore be further described herein except as required to point out modifications, and improvements in the sulfonation method which are employed in connection with the sulfonation of the higher viscosity stocks from which the preferred sulfonic acids of this invention are obtained. Methods of sulfonation which are particularly applicable to the preparation of the high molecular weight sulfonic acids of this invention are described in detail in the specific examples presented herein.

In preparing a typical hydrocarbon substituted guanidine or biguanide sulfonate salt, a bright stock is obtained from Western paraffinic crude oil by conventional procedure. A suitable paraffinic crude oil is topped to remove gas oil and lighter fractions leaving a long residuum which is solvent treated, as for example, with a mixed solvent comprising propane and phenol. The raffinate from the solvent-treatment is dewaxed and subsequently vacuum distilled to remove lower viscosity lubricating oil fractions leaving a residual oil which is clarified as by clay treatment. The resulting bright stock is sulfonated by treatment with 45% to 50% by weight of 15% fuming sulfuric acid, the contacting being effected at a temperature between about 110 and 120° F., for a period of about 15 to about 60 minutes. Preferably this contacting is effected in the presence of a low molecular weight paraffinic naphtha having a boiling range between about 150° F. and 275° F. To the resulting sulfonated product is added a small amount of water, approximately one-fourth volume per volume of bright stock employed, and the mixture permitted to settle. The aqueous phase is separated and the oil phase neutralized by the addition of aqueous sodium hydroxide such as 20% aqueous sodium hydroxide. Following neutralization the reaction mixture is permitted to settle and the aqueous phase containing inorganic salts is discarded. The neutralized product is then evaporated to recover solvent naphtha and dehydrated by heating to approximately 325° F. Following this treatment the heated product is clarified by filtration through filter aid or it may be cooled and diluted with a light petroleum naphtha and subsequently filtered at ordinary temperatures. In the latter case it

is necessary to remove solvent by topping. The sulfate ash content of products prepared in this manner are usually between about 2.0% and 5.0%. Such products are oil solutions of high molecular weight sodium sulfonates which will contain between about 10% and 30% by weight of sodium sulfonate.

A typical detergent salt of this invention is prepared from a sodium sulfonate concentrate such as the one described above by treating the concentrate with, for example, phenyl biguanide hydrochloride. In this reaction the sodium sulfonate present in the oil concentrate is converted to phenyl biguanide sulfonate. This metathesis reaction is preferably effected in an aqueous alcoholic solution. Thus approximately equal volumes of the sulfonate concentrate and water, to which is added approximately one-fourth volume of isopropanol per volume of water, is reacted with an aqueous solution of approximately 10% excess phenyl biguanide hydrochloride. The mixture is agitated for approximately one hour. At this time sufficient isopropanol is added to the mixture to break the emulsion which is formed during the mixing and the resulting reaction mixture is permitted to settle. The aqueous phase is discarded and the oil phase is washed with hot water containing the small amounts of phenyl biguanide hydrochloride and finally with hot water. The water-washed oil phase is then dehydrated and filtered at approximately 325° F. Products obtained in this manner are found to be substantially free from metal ion as indicated by sulfate ash contents of about 0.1% or less. A typical nitrogen content of such a product is 2.4% by weight.

In preparing the lubricating oils of this invention the oil concentrate of the substituted guanidine or biguanide sulfonate, which sulfonates may be prepared in the manner indicated above for phenyl biguanide sulfonate, is added to mineral lubricating oil of the desired characteristics in substantially any proportion. Generally between about 5% and about 50% by weight of the oil concentrate of the non-metal sulfonate will be employed in preparing the final lubricating oil. The finished oils will generally contain from 0.5 to 10 or 15% by weight of the non-metal sulfonates.

Although mineral lubricating oils containing the guanidine or biguanide sulfonates described herein have good detergency and improved anti-corrosion characteristics as compared with the base oil, it is generally desirable, where it is essential that the final oil have good anti-corrosion and/or good anti-oxidation characteristics, to incorporate small amounts in the order of about 0.1% to 5% by weight of an anti-corrosion and/or anti-oxidation agent which cooperate with the detergent of this invention to produce an oil having high detergency, high anti-corrosion characteristics, and high oxidation resistance. Desirably the anti-corrosion agent or anti-oxidation agent will be one which does not contain metal, however, since the proportion of such agents is generally low as compared with detergent, it is possible to use metal salts in the supplemental agents without imparting an undesirably high metal content to final lubricating oil.

Anti-corrosion agents and oxidation inhibitors which have been found to cooperate with the detergent of this invention in that they enhance the detergent effect of the guanidine and biguanide sulfonates and at the same time greatly improve the anti-corrosion characteristics of the oil, include the sulfurized and phosphosulfurized terpenes and esters such as alkyl esters of such phosphosulfurized terpenes. Such phosphosulfurized terpenes are prepared by reacting a terpene or mixtures of terpenes with phosphorus pentasulfide, trisulfide or the like at elevated temperatures. The resulting product may be used as such or may be esterified with an alcohol such as an aliphatic or cycloaliphatic alcohol and the resulting esterified compound may be employed.

Another class of compounds which may be employed

to reduce corrosion is the group of compounds commonly referred to as hindered phenols. Such phenols are those containing hydrocarbon substituents in at least the 2 and 4 positions in the ring and the preferred phenols contain hydrocarbon substituents in at least the 2, 4 and 6 positions. Typical of this group of compounds is 2, 6-ditertiary butyl-4-methyl phenol.

Another class of compounds which may be employed to reduce corrosion of the lubricating oils of this invention is the group generally referred to as phenol sulfides. These compounds and their method of preparation are shown in U. S. Patent No. 2,139,321 and include the oil-soluble hydrocarbon substituted phenol sulfides. This group includes the simple sulfides or thioethers of the alkyl phenols as well as the disulfides. Examples include amyl phenol sulfide, butyl phenol sulfide and the like.

Still another class of compounds is the class represented by alizarin, quinizarin and anthragallol. This class consists of the substituted quinones, naphtha quinones and anthraquinones.

Another class of compounds having the desired properties is the class represented by the alkyl gallates such as particularly lauryl gallate. This class includes the alcohol esters of trihydroxy benzoic acid in addition to the lauryl compounds. Other derivatives may be employed such as stearyl gallate, oleyl gallate, propyl gallate, butyl gallate, hexyl gallate, octyl gallate and like compounds.

The above compounds which are either anti-corrosion agents or anti-oxidant, but which in either case tend to prevent corrosion of corrosion-sensitive bearings in internal combustion engines are all of the ashless or non-metal type. As indicated herein it is within the scope of this invention to employ metal salts as anti-corrosion agents. Metal salts which may be employed include the polyvalent metal salts of phenol sulfides and particularly the alkaline earth metal salts of phenol sulfides such as are described in U. S. Patent No. 2,362,289. Typical of these salts are calcium salt of tertiary amyl phenol sulfide.

Another class of anti-corrosion agents is the metal thiophosphates such as those prepared by reacting P_2S_5 with an alcohol or a phenol. The method of preparing these salts and salts which may be employed are disclosed in U. S. Patent No. 2,364,284. The preferred alcohol and phenol are the monohydroxy organic compounds where the organic group comprises an alkyl, cycloalkyl, aryl, aralkyl, or alkaryl radical. Metals such as the alkaline earth metals, calcium, strontium, barium and magnesium, and the polyvalent metals, zinc, nickel, aluminum, and the like, may be employed in preparing the metal thiophosphates.

Another class of metal compounds which may be employed includes the metal alkyl substituted dithiocarbamates. A particular example which is found to be of value is the nickel dihexyl dithiocarbamate.

Methods which have been employed to evaluate the lubricating compositions of this invention include various accelerated engine tests using standard test engines. These tests have been run on lubricating oils with and without the addition of the ashless detergents of this invention. Tests have been carried out in a single cylinder Caterpillar diesel standard test engine and under two different sets of conditions in Lauson single cylinder test engines.

In carrying out the Lauson engine test under high temperature conditions, which test will be referred to herein as the high temperature Lauson engine test, the engine is operated for a total of 60 hours under a load of about 3.5 horsepower with a coolant temperature of about 295° F., and an oil temperature of about 280° F. At the end of the test, the cleanliness of the engine is observed and given a numerical "detergency rating" between zero and 100%, where 100% indicates a perfectly clean engine. Thus a detergency rating of 100 would indicate that there were substantially no lacquer or varnish-like deposits in the engine. In this test the corrosivity of the oil being

examined is measured by determining the loss in weight of corrosion-sensitive bearings of the copper-lead type after 20, 40 and 60 hours of operation. When it is observed that corrosion is extremely severe at the 20 or 40 hour examination, indicating that bearing failure might occur during the next 20-hour period of operation, the bearings are removed and replaced with babbitt bearings in order to complete the 60-hour test.

In carrying out the Lauson engine test under low temperature conditions, which test will be referred to herein as the low temperature Lauson engine test, the engine is operated for a total of 72 hours under a load of about 2.4 horsepower with a coolant temperature of 160° F. and an oil temperature of 150° F. This test is employed to determine the detergency of an oil and the detergency is rated in the manner described above in connection with the high temperature Lauson engine test. No attempt is made in this test to determine corrosivity. The bearings employed are of the babbitt type.

In the Caterpillar engine test made in the single cylinder Caterpillar engine the engine is operated for a period of 120 hours under a load of 19.8 horsepower with a coolant temperature of 175° F. and an oil temperature of about 145° F. At the end of the test the numerical "detergency rating" is assigned. The method of rating is similar to that employed in the Lauson engine tests and 100% indicates a completely clean engine.

The following examples will illustrate methods of preparation of sulfonic acids from high viscosity mineral oil fractions, methods of preparation of hydrocarbon substituted guanidine and biguanide sulfonates and will illustrate oils containing various non-metal sulfonates of this invention and their effectiveness in internal combustion engines.

Example I

A bright stock sulfonate was prepared by sulfonating a California bright stock according to the method outlined below. The bright stock employed was obtained by topping a waxy paraffnic California crude oil to remove gas oil and lighter fractions to produce a long residuum. This residuum was solvent treated in a conventional manner with a solvent comprising propane, phenol and a mixture of cresols and the raffinate from the solvent treatment was dewaxed in a conventional manner. The dewaxed raffinate was then vacuum distilled to obtain a residuum having a viscosity at 210° F. of approximately 185 seconds. This residuum was clay treated and filtered. The resulting bright stock had a viscosity index of 85 and a viscosity 210° F. of 185.

A mixture of 800 grams of the bright stock and 800 ml. of a light paraffinic naphtha having a boiling range between about 150° F. and 210° F. was vigorously agitated at room temperature and 200 ml. of 15% fuming sulfuric acid was added over a period of approximately five minutes. The temperature rose spontaneously to about 120° F. Agitation was continued for approximately 45 minutes, at which time 200 ml. of water was added and the temperature increased to 155° F. The mixture was allowed to settle for 18 hours. After settling, the aqueous phase was removed and 55 ml. of isopropanol was added to the oil phase. Neutralization was effected by adding about 100 ml. of 20% aqueous sodium hydroxide solution and agitating the mixture. Following neutralization the batch was permitted to settle for 18 hours and the aqueous phase then discarded. The oil phase was freed of solvents and dehydrated by heating to 325° F. and stripping with natural gas. The resulting product was then filtered through a filter aid at about 325° F. to effect clarification.

The product produced as above consists of an oil concentrate of sodium bright stock sulfonate containing approximately 20% by weight of sodium sulfonate. It has a sulfate ash of approximately 4.1%.

Example II

Example I was repeated. However, in this instance 100 ml. of water was added to the sulfonation mixture in place of the 200 ml. portion used in Example I. In this case the spent acid separated more easily from the oil solution of sulfonic acids and a somewhat larger amount of sodium hydroxide solution was required to effect complete neutralization. Approximately 150 ml. of 20% aqueous sodium hydroxide was required. The product contains approximately 21% by weight of sodium sulfonate and has a sulfate ash of approximately 4.

Example III

An oil concentrate of phenyl biguanide sulfonate was prepared from the bright stock sulfonate produced in Example I. A mixture of 400 grams of the sodium bright stock sulfonate from Example I, 400 ml. of water and 100 ml. of isopropanol was heated and agitated at 180° F. and a solution consisting of 50 grams (approximately 10% excess) of phenyl biguanide hydrochloride in 700 ml. of hot water was added. Agitation was continued for 40 minutes and then 200 ml. of isopropanol was added. The mixture was allowed to settle for about 15 hours. The separated aqueous phase was withdrawn and discarded and the oil phase containing phenyl biguanide sulfonate was washed with 1 liter of hot water containing 5 grams of phenyl biguanide hydrochloride. A small amount of isopropanol was added to assist in breaking the emulsion which formed during the water washing. After settling the aqueous phase was withdrawn and the oil phase washed with 1 liter of hot water. Following the latter water wash, the oil phase was dehydrated and filtered through a small amount of filter aid at 325° F. The metathesis was judged to be essentially complete since the sulfate ash of the final product was 0.01.

The resulting product had a sulfur content of 1.67% and a nitrogen content of 2.35% and contained approximately 22% of the phenyl biguanide sulfonate.

A lubricating oil was prepared by dissolving 15% of the phenyl biguanide sulfonate oil concentrate in a mineral lubricating oil of SAE 30 grade having a viscosity index of 85. This oil which contained approximately 3.3% by weight of the additive was evaluated in the high temperature Lauson engine test and for comparison similar tests were made on the base oil and on the oil containing the phenyl biguanide sulfonate together with (1) 0.5% by weight of a commercial ashless anticorrosion agent containing phosphorus and sulfur and being an ester of a phosphosulfurized terpene, (2) 0.5% by weight of zinc, dicyclohexyl, dithiophosphate, and (3) 1% by weight of lauryl gallate.

The results of these Lauson engine tests are shown in the following table:

Oil No.	Composition	Detergency, Percent	Bearing Weight Loss at—		
			20 hrs.	40 hrs.	60 hrs.
A	Base Oil	40	93	449	597
B	Base Oil+3.3% Phenyl Biguanide Sulfonate.	70	51	139	319
C	Oil B+0.5% Phosphosulfurized Terpene Ester.	74	25	53	100
D	Oil B+0.5% Zn dicyclohexyl dithiophosphate.	72	46	60	72
E	Oil B+1% lauryl gallate	73	11	15	17

A lubricating oil was prepared containing 3.3% by weight of the phenyl biguanide sulfonate and 0.2% by weight of the commercial phosphosulfurized terpene ester in an SAE 30 solvent-treated Western paraffinic lubricating oil. This oil was tested in the Caterpillar test engine and found to have a detergency rating of 98% after 120 hours of operation. For comparison a Caterpillar engine

test on the base oil showed a detergency rating of 49% after the same period of operation.

Example IV

A phenyl biguanide sulfonate oil concentrate was prepared from a commercial petroleum sulfonate having an average molecular weight of about 470. An emulsion was prepared by heating to 180° F. and agitating a mixture of 1,000 grams of the commercial sulfonate (approximately 60% sodium mahogany sulfonate in mineral oil) 2,000 ml. of water and 500 ml. of isopropanol. To this heated emulsion was added a solution of 300 grams of phenyl biguanide hydrochloride in 4,000 ml. of water heated to about 180° F. and the resulting mixture was agitated for 15 minutes. After settling for 16 hours the aqueous phase was withdrawn and discarded and the oil phase was washed with 4,000 ml. of hot water containing 30 grams of phenyl biguanide hydrochloride. After settling and removal of the aqueous phase the oil phase was again washed with 4,000 ml. of hot water. To the resulting water washed product was added 1,000 grams of an SAE 20 solvent treated Western paraffinic mineral lubricating oil having a viscosity index of about 85 and the mixture was dehydrated by heating to 325° F. and filtered.

The clarified concentrate containing approximately 35% by weight of phenyl biguanide sulfonate had a nitrogen content of 3.83% and a sulfur content of 2.26%.

A mineral lubricating oil prepared by dissolving 10% by weight of the above clarified concentrate in a lubricating oil, was tested in a Lauson single cylinder test engine under low temperature conditions as described hereinabove and found to have a detergency rating of 93%. A comparative test on the oil without additives shows the oil to have a detergency of about 57%.

A second lubricating oil was prepared by dissolving 10% of the above clarified concentrate and 1% of lauryl gallate in a portion of the same SAE 30 mineral lubricating oil. This product had a detergency rating of 95%.

Example V

A concentrate of the phenyl guanidine sulfonate in mineral lubricating oil was prepared from the same commercial sodium mahogany sulfonate employed in Example IV. In this case 2,000 grams of the commercial sulfonate, 4,000 ml. of water and 1,000 ml. of isopropanol was agitated at 180° F. and to this mixture was added 520 grams of phenyl guanidine carbonate. Agitation was continued at 180° F. for 1 hour and the mixture permitted to settle. The aqueous phase was withdrawn and discarded and the oil phase was washed with 6,000 ml. of hot water (180° F.) containing 100 grams of phenyl guanidine carbonate. This mixture was agitated for one hour and then allowed to settle. The aqueous phase was discarded and the mixture then washed with 6,000 ml. of hot water. To the resulting water-washed product was added 2,000 ml. of an SAE 20 solvent-treated paraffinic Western mineral lubricating oil and the resulting mixture was dehydrated and filtered at 325° F. The resulting product contains approximately 30% by weight of phenyl guanidine sulfonate. It has a sulfate ash content of 0.07%, sulfur content of 2.05%, and a nitrogen content of 2.80%.

A mineral lubricating oil was prepared by dissolving 15% by weight of the above oil concentrate in a SAE 30 mineral lubricating oil of the type employed in Example IV. The resulting oil has good detergency and improved anti-corrosion characteristics when employed in internal combustion engines and operates satisfactorily in automotive engines.

Example VI

A phenyl guanidine sulfonate was prepared from the sodium bright stock sulfonate prepared in Example I using the procedure of Example V. In this case the product consisted of an oil concentrate containing approximately 22% by weight of the phenyl guanidine sulfonate.

A lubricating oil was prepared by dissolving 18% by weight of the oil concentrate in an SAE 30 solvent-treated lubricating oil to produce an oil containing about 4% by weight of phenyl guanidine bright stock sulfonate. This oil was tested in a Lauson engine under low and high temperature conditions. The detergency in the low temperature test was 97% and in the high temperature test was 78% as compared with detergency ratings of 57% and 40%, respectively, for the base oil in these same tests. Bearing weight losses at 20, 40, and 60 hours were 44 mg., 97 mg., and 161 mg., respectively, in the high temperature test as compared with losses of 93 mg., 449 mg., and 597 mg. for the base oil.

Example VII

On oil concentrate of dixylyl biguanide sulfonate was prepared following the procedure outlined in Example III using dixylyl biguanide hydrochloride in place of the phenyl compound. The product, when dissolved in a paraffinic mineral lubricating oil to give a sulfonate conten of about 8% by weight produces an oil having exceptional detergency characteristics.

Example VIII

An oil concentrate of diphenyl biguanide sulfonate prepared by reacting diphenyl biguanide hydrochloride with sodium bright stock sulfonate as described in Example I when dissolved in an SAE 30 naphthenic lubricating oil to give a finished oil containing 2% by weight of diphenyl biguanide sulfonate, is found to operate satisfactorily in automotive engines.

Example IX

An oil concentrate of hexyl guanidine sulfonate is prepared according to the procedure described in Example V using hexyl guanidine in place of phenyl guanidine and bright stock sulfonate of Example I in place of the commercial sulfonate. A lubricating oil containing 25% of the above product has good detergency characteristics as indicated by a low temperature Lauson engine test.

Example X

An oil concentrate of lauryl guanidine sulfonate, prepared by reacting 2,000 grams of a commercial sodium sulfonate oil concentrate with 480 grams of lauryl guanidine hydrochloride in solution in 4,000 ml. of water and 1,000 ml. of isopropyl alcohol and washing the product free of inorganic salts, when added to mineral lubricating oil in quantities sufficient to impart a sulfonate content of about 5% by weight produces an oil having excellent detergency properties and fair anticorrosion characteristics. The detergency and anticorrosion characteristics are both found to be improved by incorporating in the oil approximately 1% by weight of octylphenol sulfide.

Example XI

An oil concentrate of trihexyl biguanide bright stock sulfonate prepared by the procedure outlined in Example III when added to mineral lubricating oil to give an oil containing approximately 6% by weight of the sulfonate produces an oil having good detergency in the low temperature Lauson engine test.

Example XII

Example XI repeated using methylcyclohexyl bigaunide gives lubricating oils comparable with that of Example XI. In this case a paraffinic lubricating oil containing 6.5% of the methylcyclohexyl biguanide sulfonate has excellent detergency in the low temperature Lauson engine test.

The foregoing description and examples of this invention are not to be taken as limiting since variations

may be made by those skilled in the art without departing from the spirit or the scope of the following claims.

I claim:

1. A composition of matter adapted for addition to lubricating oil consisting essentially of a mineral oil concentrate containing not more than about 35% of phenyl biguanide oil-soluble petroleum sulfonate.

2. A composition according to claim 1 in which said oil-soluble petroleum sulfonate is a bright stock sulfonate.

3. A mineral lubricating oil having detergent characteristics consisting essentially of a mineral lubricating oil containing small amounts, between about 0.5% and 15% by weight, sufficient to impart detergency characteristics to said oil of phenyl biguanide oil-soluble petroleum sulfonate.

4. A lubricating oil according to claim 3 wherein said oil-soluble petroleum sulfonate is a bright stock sulfonate.

5. A lubricating oil according to claim 3 containing also between about 0.1% and about 5% by weight of a phosphosulfurized terpene ester.

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