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LUBRICATING OIL COMPOSITION

Loren L. Neff, Long Beach, Calif., assignor to
Union Oil Company of California, Los Angeles,
Calif., a corporation of California.

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This invention relates to mineral lubricating oils which have been modified by the addition of constituents which impart to the oils special characteristics adapting them to use in diesel engines and the like and for use in any internal combustion engine where conditions of use are so severe that ordinary lubricating oils are not satisfactory. It relates also to the addition agents themselves and to methods for preparing the agents as well as to oil concentrates of the addition agents which are convenient to handle in that they are readily dissolved and/or dispersed in lubricating oil to prepare the final lubricating oil compositions.

It is well known that ordinary mineral lubricating oil will not operate satisfactorily in internal combustion engines, particularly of the diesel engine type, where conditions of operation are such as to cause sludging, formation of resinous and varnish-like deposits on engine parts such as pistons, rings and the like and cause deterioration or corrosion of corrosion-sensitive bearings. Various addition agents have been suggested and, in fact, are being used which tend to overcome the undesirable features referred to above. However, generally it is found that at least two and sometimes three or more different agents must be added in order to obtain all of the desired characteristics in the finished lubricating oil. Thus, it is found that certain additives, referred to as detergents, tend to prevent the accumulation of resinous and lacquer-like deposits in the engine. However, these additives alone do not impart anticorrosion characteristics to the lubricating oil and it is observed that in operating an engine with an oil containing an additive of this character that, although the engine remains "clean," i. e., remains free from resinous and lacquer-like deposits, the bearings will show excessive wear and/or corrosion. It is also found that other additives which may be referred to as anticorrosion agents impart to the oil the ability to prevent excessive wear and/or corrosion of bearings. Combinations of these two types of additives have given oils of good quality. It is observed, however, that the detergent additive usually decreases the effectiveness of the anticorrosion additive and, conversely, the anticorrosion additive often tends to decrease the effectiveness of the detergent additive so that in order to obtain satisfactory anticorrosion characteristics in a given oil it is generally necessary to add a larger amount of anticorrosion agent if a detergent additive is to be included in the composition than would be required if the detergent additive was

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not included. The same observation is made in regard to the detergency additive; quite often a larger proportion of detergency additive is required if it is to be used in conjunction with an anticorrosion additive than if it were to be employed by itself. The requirements of larger amounts of additives is not serious in oils which are satisfactory for automotive engines or even ordinary diesel engines operated under the usual conditions where the proportion of additive is normally rather low, but it is important in oils suitable for use in the recently developed supercharged diesel engines which operate under far more severe conditions than ordinary diesel engines. The oil temperatures and general engine temperatures are considerably higher and oil deterioration rates are thus greatly increased. Moreover, the present trend is toward the use of diesel fuels containing sulfur in quantities such that corrosion and wear in the engines with low additive content oils is excessive. In order to produce oils which will operate in the supercharged diesel engines using high sulfur content fuels it is found that as much as 10 or 20% or more of additive materials must be employed, particularly where frequent oil changes are not conveniently made. Where such high proportions of additives are required any saving in additive cost or in the amount of additive required to give the desired protection becomes extremely important.

It is an object of this invention to prepare a lubricating oil containing a single additive material which will impart both detergency and anticorrosion characteristics to an oil and it is a further object of the invention to prepare a lubricating oil containing such an additive which will have the desirable detergency and anticorrosion characteristics and contain less total additive material than an oil of similar quality containing two or more separate additives.

It is a further object of this invention to prepare a bifunctional lubricating oil additive, i. e., one having the ability to impart detergency and anticorrosion characteristics to a lubricating oil, which additive, when used in moderate amounts, has the ability to impart sufficient detergency and anticorrosion characteristics to a given mineral oil for most services and which, when added to mineral lubricating oil in larger amounts, will produce an oil of outstanding quality.

It is found that these objects can be obtained by reacting a phenolic material, preferably a substituted phenol, with a low molecular weight aldehyde, as for example formaldehyde, in the

presence of sulfonic acid and neutralizing the resulting product with a metal base to produce the metal salt of the reaction product. This metal salt, which is oil-soluble, may be dissolved in mineral lubricating oil to produce an oil having exceptional detergency and anticorrosion characteristics. The preparation of the reaction product and of the metal salt may be effected in the presence or absence of mineral oil and if mineral oil is employed it will generally be of lubricating oil grade. If the preparation is carried out in the absence of mineral oil it is generally effected in the presence of a light petroleum thinner or naphtha and the naphtha vaporized at the completion of the reaction, or preferably it will be vaporized after the metal salt has been formed. In those cases in which the reaction is effected in the presence of mineral oil the resulting product is an oil concentrate of the reaction product and an oil concentrate of the product prepared in the absence of mineral oil may be obtained by simply mixing the product, before or after neutralization, with mineral oil, preferably at elevated temperatures, to increase the rate of solution and/or dispersion. In this case the petroleum thinner, if employed, may be volatilized before or after the addition of mineral lubricating oil. The resulting oil-soluble metal salt or the oil concentrate of the metal salt may be dissolved in mineral lubricating oil in amounts ranging from about 0.5% to 10% or even as much as 15 or 20% of the salt to produce the lubricating oils of this invention. The higher percentages indicated are or may be used in preparing lubricating oils for use under extreme service conditions, such as are encountered in the high output supercharged diesel engines.

In preparing lubricating oil additives of this invention one equivalent of a phenolic compound, such as octyl phenol, is mixed with between about 0.05 and 2 or 3 equivalents of sulfonic acids such as mahogany sulfonic acids and a volume of oil approximately equal to the volume of sulfonic acids or more, as desired, to a temperature of about 175° F. to 210° F. An aldehyde such as formaldehyde is slowly added to the mixture with stirring over a period of a few minutes up to an hour or more, depending upon the aldehyde employed, the size of the batch and the temperature. Preferably formaldehyde is employed as a 40% solution in water (formalin). The product is heated and stirred for 2 to 3 hours to effect condensation and the resulting product is found to be acidic and capable of forming salts with inorganic bases. The acid product, which may be referred to as a modified phenol formaldehyde resin, is converted into its metal salt by treatment with a metal base, as for example a metal oxide or hydroxide, and the resulting metal salt, which is oil-soluble, constitutes the additive of this invention.

In carrying out the condensation reaction, generally the temperature will be maintained between about 150° and 250° F. or 300° F., the range of 175° to 210° F. or 220° F. being preferred. In case water is employed, as it is particularly when using formalin, the temperature is maintained below about 212° F. until the addition of formalin has been completed and then slowly increased to 225° F. to 275° F. over a period of 2 to 3 hours. Moreover, it is generally preferred to mix the desired quantity of sulfonic acids and phenols together with the desired quantity of petroleum thinner and/or mineral lubricating oil and heat the mixture to a temperature of

about 175° F. to 200° F. To the heated mixture is then added the desired aldehyde, preferably with small amounts of water, the addition taking place relatively slowly and may be continuous or intermittent, depending upon the equipment available. The amount of aldehyde to be added will generally be around 1.25 to 2 equivalents per equivalent of phenol. Smaller amounts tend to produce resins containing uncondensed or unreacted phenolic molecules and larger amounts appear to be unnecessary to produce the desired condensation.

It is to be noted that the above preparation is carried out in the absence of added catalysts. Normally, in reacting a phenolic compound such as octyl phenol with formaldehyde, either an acid or basic catalyst is employed in order to facilitate the condensation. The usual condensation product is referred to as a phenol-aldehyde resin and is believed to contain in the neighborhood of about 4 or 5 phenolic residues per molecule. The preparation of phenol-aldehyde resins is well known in the art and has been described in U. S. Patents Nos. 2,250,188 and 2,375,222. In the preparation of these resins either a mineral acid catalyst, such as HCl or H₂SO₄ or the like or a basic catalyst, such as calcium hydroxide, sodium hydroxide or the like, has been employed. The basic catalysts are generally used when it is desired to produce the salt of the phenol-aldehyde resin and when the acid resin itself is the desired product a mineral acid has generally been employed as the catalytic agent. One reason that acid catalysts are not employed when it is desired to produce metal salts of the resulting phenolaldehyde resins is that the resins produced with the acid catalysts apparently do not contain as many phenolic hydroxyl groups as do the resins produced using a basic catalyst. At least the acid catalyzed resins are not capable of reacting with as much base and do not form salts with as high a metal content as do the base catalyzed resins. Thus, when a resin produced using HCl as the catalyst is neutralized with calcium hydroxide, for example, the amount of calcium taken up by the resin is far less than that taken up by a resin produced using calcium hydroxide as the catalyst. Moreover, the condensation reaction is generally slower using mineral acids than when bases are employed.

It has now been found that sulfonic acids may be employed to catalyze the condensation reaction between a substituted phenol and formaldehyde to produce a resin having the ability to react with relatively high proportions of a base. Apparently the condensation reaction occurring in the presence of a sulfonic acid catalyst more nearly corresponds to that reaction which takes place with basic catalysts and overcomes the deficiencies of the usual acid catalyzed resin. Where it is desired merely to produce a resin of a phenol and an aldehyde, for example, relatively small amounts of sulfonic acids suffice as catalytic agent, i. e., amounts in the range of 0.5 to 5% by weight of sulfonic acids based on the phenol, appear to catalyze the condensation reaction, and thus it is possible to produce acid phenol-aldehyde resins having a relatively high acid value by employing sulfonic acids as the catalytic agent. Such resins have value per se in the paint and varnish industry as components of paints, varnishes and the like. Moreover, they may be converted to the desired metal salt and employed in lubricating oils as anticorrosion agents and the like.

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It is found, further, that by using relatively larger proportions of sulfonic acids during the condensation reaction the resulting acidic product apparently retains the acidity due to sulfonic acid as well as most of the acidity of the original phenol, which acidity is enhanced during condensation, and that the acid resins produced in which sulfonic acids are incorporated, when neutralized with inorganic bases to produce the corresponding metal salts, are unusually valuable lubricating oil addition agents imparting a high degree of detergency and anticorrosion and even antiwear characteristics to the mineral lubricating oil. The amount of sulfonic acid to be employed may be varied depending upon the character of the product desired but will generally be between 0.05 and 3 equivalents of sulfonic acids per equivalent of phenol. If the resulting oil-soluble metal salt is to be employed in an oil in which a very high degree of detergency is required and where only moderate anticorrosion characteristics are necessary, the ratio of sulfonic acids to phenol in the reaction mixture may be as high as 2 or even 3 to 1 on an equivalency or molecular weight basis. If, on the other hand, the desired oil is one having exceptional anticorrosion and antiwear characteristics and detergency is of secondary importance, amounts of sulfonic acid as low as 0.05 to 0.2 equivalent of sulfonic acid per equivalent of phenol may be employed in preparing the modified resin. Generally around 0.2 to 2.0 equivalents of sulfonic acids per equivalent of phenol will be employed to give a product which, when neutralized and incorporated in mineral oil, will give a balanced lubricating oil, i. e., one having the desired detergency and anticorrosion characteristics for most purposes.

The sulfonic acids to be employed are preferably the so-called mahogany or oil-soluble sulfonic acids which are obtained by treating mineral oil fractions and especially fractions of lubricating oil grade with sulfonating agents such as sulfuric acid, chlorosulfonic acid and the like. However, it is found that mixtures of mahogany and green sulfonic acids which may be obtained by neutralizing the total sulfonation product, i. e., both the water-soluble and oil-soluble acids obtained in sulfonating a lubricating oil fraction of petroleum, for example, and separating the mixed mahogany and green acids from their soaps by acidification with a mineral acid. It is found that such mixtures of mahogany and green acids, when employed in the manner described herein, form oil-soluble metal salts which have the desirable characteristics. Moreover, in some instances, particularly where the proportion of sulfonic acid is to be relatively low, i. e., such as 0.2 to 1 equivalent of sulfonic acid per equivalent of phenol used in the preparation of the modified resin, it is possible to use green acids and still obtain oil-soluble metal salts of the resulting resins. Since, generally, the metal salts of green sulfonic acids are not appreciably oil-soluble, it is presumed that the phenol-aldehyde resin has a solubilizing effect on the sulfonic acids or that the sulfonic acids enter into the reaction, producing a complex or modified phenol-aldehyde resin in which the sulfonic acid molecules modify the usual resin structure and actually form a part of the resin structure. The latter explanation is believed to be the proper one for the reason just presented as well as for the reason that the products of this invention produce oils having higher detergency ratings and/or higher anti-

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corrosion and antiwear characteristics per given quantity of additive than do oils containing the phenol-formaldehyde resin salts and sulfonic acid salts prepared separately. The methods of preparing both green and mahogany acids are well known and need not be further discussed.

Phenols which may be employed in the preparation of the modified resins of this invention include those phenolic compounds which will produce oil-soluble resins with low molecular weight aldehydes and these include phenols with at least one substituent having at least 3 and preferably 4 or more carbon atoms. The substituent may be an alkyl group, such as butyl, isobutyl, amyl, tert. amyl as well as the normal and iso, hexyl, heptyl, octyl, nonyl, decyl, lauryl, stearyl, oleyl and like groups; cycloalkyl groups such as cyclopentyl, cyclohexyl, alkyl substituted cyclopentyl and cyclohexyl such as methylcyclohexyl, ethylcyclohexyl, dicyclohexyl and the like; an aryl group such as ethylphenyl, dimethylphenyl and aralkyl groups, as for example benzyl, and the like. In place of the single aromatic ring as in phenol, the aromatic nucleus of the phenol may be mono or dicyclic and, therefore, may be a naphthalene nucleus. Naphthalene itself may be employed although generally better oil solubility of the resulting resins are obtained with substituted naphthalene where the substituents may be any of those indicated above for phenol.

The aldehyde which is referred to herein as a lower molecular weight aldehyde is preferably formaldehyde, although aldehydes containing up to 4 or 5 carbon atoms may be employed. Thus, acetaldehyde, propionaldehyde, butyraldehyde, furfuraldehyde may be employed to produce the phenol-aldehyde resins which are usable in the preparation of the complexes of this invention. Formaldehyde is generally used as a 40% aqueous solution, however other forms may be employed. Paraformaldehyde or polymethylene oxide may be employed or trioxane, which is a trimer of formaldehyde, may be used with satisfactory results.

Inorganic bases which may be used to prepare the metal salts of the modified phenol-aldehyde resins of this invention include the basic compounds, particularly the hydroxides, hydrated oxides or oxides and, in some cases, the carbonates, of the alkaline earth metals, as for example, calcium, strontium, barium and magnesium, the alkali metals sodium, potassium and lithium and the polyvalent metals lead, tin, zinc, aluminum, copper, cadmium, mercury, vanadium, chromium, molybdenum, manganese, iron, cobalt and nickel. Generally the salts are produced by direct neutralization of the acid resin product. Thus, the acid resin directly as produced is treated with a sufficient quantity of the desired inorganic base to completely neutralize the resin. Preferably the neutralization is carried out at elevated temperatures and the inorganic base is added as a water solution or at least water is added along with the inorganic base to aid the neutralization reaction. When neutralization is complete the product is preferably heated to expel the water and the resulting product filtered to remove excess base, if present, and clarify the product. This neutralization may be effected in the presence of naphtha or other petroleum thinner where such naphtha or petroleum thinner was employed in the preparation of the acid resin and, following neutralization, the water and petroleum thinner is volatilized from the product. In some instances it may be desirable to prepare

a particular metal salt, such as a polyvalent metal salt, by first preparing an alkali metal salt, e. g., the sodium salt, and converting this salt to the desired polyvalent metal salt by metathesis. This metathesis reaction can be carried out in alcoholic solution, thus preventing hydrolysis which would occur in aqueous solution because the modified phenol-aldehyde resins are relatively weak acids. Methods of metathesis of weak acid salts are well known in the art and, therefore, need no further description here.

The oil-soluble salts of the modified phenol-aldehyde condensation products as described herein may be employed to improve the lubricating characteristics of any lubricating oil. Preferably the mineral oil to be employed will be a lubricating oil having a viscosity index as defined by Dean and Davis, *Chemical and Metallurgical Engineering*, volume 36, page 618 (1929), above about 70 such as those produced by solvent treating paraffinic base stocks. An ideal oil to be used in connection with the additives of this invention is a highly solvent treated paraffinic Western lubricating oil having a viscosity index of 85 to 95. For some purposes the lower viscosity index oils such as those having viscosity indices of below 70, such as in the range of 9 to 50, produce high quality oils when the additive is dissolved in them in amounts indicated herein.

Lubricating oils containing the oil-soluble metal salts of the modified phenol-aldehyde resins of this invention have been evaluated in Lauson single cylinder test engines operated in such a manner that the oil is subjected to severe service conditions. This test is employed to determine the corrosion tendencies of the oil and to determine the tendency for the oil to deposit resinous and lacquer-like materials in the engine. In carrying out the 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 the oil is given a numerical detergency rating between 0% and 100%, where 100% indicates a perfectly clean engine. Thus, a detergency rating of 100% would indicate that during the test with a given oil there were substantially no lacquer or varnish-like deposits within the engine. The corrosivity of the oil is measured by determining the loss in weight of corrosion-sensitive copper-lead bearings during the period of test. Generally, the bearings are removed and weighed after 20, 40 and 60 hours of operation. In those cases in which corrosion is extremely severe and there appears to be danger of engine failure due to excessive corrosion of the bearings as indicated by an examination made at the 40-hour period, the copper-lead bearings are replaced with babbit bearings in order to complete the 60-hour test. The results of such engine tests are shown in connection with some of the examples presented hereinbelow.

In order to show the value of lubricating oils containing oil-soluble metal salts of the modified phenol-aldehyde resins of this invention, additives have been prepared and lubricating oils containing these salts have been tested in Lauson engines. Moreover, for purposes of comparison lubricating oils have been prepared containing oil-soluble sulfonates alone, phenol-aldehyde resin salts which resins have not been modified by the inclusion of sulfonic acids and oils con-

taining these unmodified resin salts together with oil-soluble metal sulfonates separately prepared and incorporated in the oil, and these oils have been tested in Lauson engines. Test results on the mineral oil used in preparing the additive oils are also presented.

In the following examples the proportion of additive material is referred to in many instances on the basis of the sulfate ash content of the product or of the resulting mineral lubricating oil. The sulfate ash is a measure of the metal content of the material being tested. The term "sulfate ash" or "SO₄ ash" may be defined as the percentage of residue obtained when a weighed portion of a material is ashed or burned in the presence of sulfuric acid. Thus, if a sulfate ash determination is carried out on a composition consisting of the calcium salt of a modified phenol-aldehyde resin and oil, the sulfate ash of the composition is the amount of dry residue expressed in percentage obtained from a weighed amount of the composition after being ashed or burned in the presence of sulfuric acid. Generally the amount of oil-soluble metal salt of the modified phenol-aldehyde resin of this invention to be employed in preparing the final lubricating oil composition, indicated hereinabove as being between about 0.5% and 20% by weight, will be such that the sulfate ash of the final oil will be between about 0.1% and 6%. It is to be pointed out, however, that this value varies with the ratio of phenol to sulfonic acids in the modified resin and particularly with the equivalent weight of the metal used in preparing the metal salt. In the case of the heavier metals such as lead, the sulfate ash of the product may be as high as 8% or even 10% by weight.

Example I

A modified phenol-aldehyde resin is prepared in the following manner. Mahogany sulfonic acids are prepared from a commercial calcium sulfonate containing about 62% by volume of oil by treatment with aqueous HCl solution. The sulfonic acids are washed free from inorganic salts produced during the acidification and 500 g. of the sulfonic acids in oil (0.67 equivalent) are mixed with 500 g. (2.42 equivalents) of octyl phenol and 2580 g. of an SAE 10 solvent treated Western mineral lubricating oil having a viscosity index of 90. This mixture is heated with vigorous stirring to 175° F. and 291 ml. of 40% by volume formalin solution is added drop-wise over a period of about 15 minutes. The mixture is heated at a temperature between 175° F. and 210° F. for 2 to 3 hours and at this time an amount of calcium hydroxide equivalent to the phenol and sulfonic acid employed in the preparation of the mixture is added along with a small amount of water and the mixture heated to about 350° F. to boil out the water. The resulting mixture is filtered through filter clay using vacuum. The filtrate is a green oil solution and analysis shows it to have a sulfate ash of 4.93%, of which about 0.91% is due to the calcium salt of the sulfonic acid portion of the resin and about 4.07% is due to the calcium salt of the phenolic materials present in the resin. This corresponds to a 90% yield of calcium salt of the condensation product. Thus, the sulfate ash determination indicates that 90% of the hydroxyl groups of the original phenol used in the condensation have reacted to form the calcium salt.

A lubricating oil is prepared from the above

oil concentrate by dissolving 20 parts by weight of the oil concentrate in 80 parts by weight of an SAE 30 solvent treated Western mineral lubricating oil having a viscosity index of 90. The resulting product, having a sulfate ash of 1.00, tested in a Lauson engine is found to have a detergency of 95% and a bearing weight loss at 60 hours of 40 mg.

A second lubricating oil is prepared from the above oil concentrate by dissolving 12 parts of concentrate in 88 parts of the same mineral lubricating oil. This oil has a sulfate ash of 0.60%, of which 0.11% is due to the calcium salt of the sulfonic acid constituent of the resin complex and 0.49% is due to the calcium salt of the phenolic portion of the resin. Lauson test results are shown for this oil in the table in Example IX.

Example II

Example I is repeated using barium hydroxide in place of calcium hydroxide. The lubricating oil products are of similar quality and have substantially the same detergency rating and anti-corrosion characteristics as shown for the corresponding calcium products.

Example III

A 200 g. portion (0.97 mole) of octyl phenol is dissolved in 1.5 liters of a light paraffinic hydrocarbon thinner and a 340 g. portion of sulfonic acids (0.46 mole) as an oil concentrate prepared from commercial calcium sulfonate in oil as described in Example I is added to the phenol solution and the mixture heated to 90° F. At this time 58.4 g. (1.95 moles) of polymethylene oxide and 50 ml. of water is added. The mixture is heated and stirred under a reflux condenser at a temperature of about 145° F. for 2.5 hours. To the resulting mixture is added sufficient calcium hydroxide to neutralize the acid product and the refluxing continued for 3 hours. A water trap is then installed in the reflux line and refluxing continued until no further water is separated from the reflux. At this point the mixture is cooled, filtered through clay and the filtrate heated to 370° F. with fuel gas stripping to vaporize the thinner. The product is a green oil solution (the oil being present in the sulfonic acids employed) having a sulfate ash of 10.6%, of which 4.47% corresponds to the calcium salt of the sulfonic acids used in the preparation, and 6.13% corresponds to the calcium salt of the phenolic portion of the condensation product.

A lubricating oil is prepared by dissolving 5 parts of the above calcium salt in 95 parts by weight of an SAE 30 mineral lubricating oil as described in Example I. This oil has a sulfate ash of 0.53%, 0.22% due to sulfonate portion of the resin and 0.31% due to phenolic portion of the resin. The results of a Lauson engine test on this oil are shown in the table in Example IX for purposes of comparison with other lubricating oils.

Example IV

For purposes of comparison with oils of this invention a phenol-formaldehyde resin salt is prepared by conventional methods as follows: A 300 g. (1.46 moles) portion of octyl phenol is dissolved in 3 liters of a low boiling hydrocarbon solvent and to this solution is added 87.5 g. (2.92 moles) of polymethylene oxide and 50 ml. of water and the mixture heated to about 105° F.

At this time 54 g. (1.46 equivalents) of calcium hydroxide is added slowly with rapid stirring and the mixture heated to about 175° F. for 3 hours under a reflux condenser, at which temperature rapid refluxing occurs. A water trap is installed in the reflux line and refluxing continued until no more water is obtained in the trap. The resulting mixture is cooled and filtered through clay and the product, which is a clear orange filtrate, is topped to a temperature of about 300° F. to remove the solvent. The final product has a sulfate ash of 16.8%, corresponding to a yield of calcium salt of 58% of the theoretical based on the phenol originally employed.

A lubricating oil is prepared by dissolving 1.84 parts by weight of the above calcium salt in 98.16 parts by weight of an SAE 30 lubricating oil described in Example I. A Lauson engine test was made on this oil which had a sulfate ash content of 0.31% and the results are shown in the table presented in Example IX.

Example V

A second phenol-formaldehyde resin salt is prepared by conventional methods in oil solution for purposes of comparison with the additives of this invention. In this case, 500 g. of octyl phenol is dissolved in 2580 g. of an SAE 10 mineral lubricating oil. The mixture is heated and stirred until the temperature reaches 175° F. At this time 94 g. of calcium hydroxide is added and 291 ml. of 40% formalin is added dropwise over a 15-minute period. When the addition of formalin is complete the temperature is gradually raised to 350° F. over a period of 5 hours. The product is filtered hot and the filtrate is a greenish-colored oil solution having a sulfate ash of 4.54%. This corresponds to an 86% yield of the calcium salt based on the original phenol content of the mixture.

A lubricating oil is prepared having a sulfate ash of 0.31% by dissolving 6.8 parts by weight of the product in 93.4 parts by weight of the SAE 30 mineral lubricating oil described in Example I. The results of a Lauson engine test on this oil are given in the table in Example IX.

Example VI

A mineral lubricating oil is prepared by dissolving 3.33 parts by weight of the commercial calcium sulfonate referred to in Example I in 96.67 parts by weight of an SAE 30 mineral lubricating oil as described in Example I. The resulting oil has a sulfate ash of 0.22%. The results of a Lauson engine test on this oil are given in the table in Example IX.

Example VII

A lubricating oil is prepared by dissolving 3.33 parts by weight of the commercial calcium sulfonate referred to in Example I and 6.8 parts by weight of the product of Example V in 89.87 parts by weight of the SAE 30 mineral lubricating oil described in Example I. The results of a Lauson engine test on this oil are shown in the table in Example IX.

Example VIII

For purposes of comparison a conventional phenol-aldehyde resin is prepared by dissolving 500 g. (2.43 moles) of octyl phenol in 2580 g. of an SAE 10 mineral lubricating oil and bubbling HCl gas through the mixture continuously while add-

ing 291 ml. (3.64 moles) of 40% by volume of formalin solution and during a subsequent heating period of 5 hours. During the heating period, the temperature, which is originally about 175° F. is gradually increased to about 340° F. The resulting product is neutralized with calcium hydroxide and a small amount of water and subsequently filtered through clay. The filtrate is a brown oil solution with a greenish cast and has a sulfate ash of 1.0%. This corresponds to a yield of about 19% based on the phenol employed in the preparation of the resin.

A lubricating oil is prepared from this product by dissolving 24 parts by weight of the above product and 3.33 parts by weight of the calcium sulfonate described in Example I in 72.67 parts by weight of the SAE 30 mineral lubricating oil of Example I. Lauson engine test results on this oil are shown in the table in Example IX.

Example IX

The results of Lauson engine tests made on a 90 V. I. Western mineral lubricating oil of SAE 30 grade and on the oils of Examples I and III to VIII inclusive which were prepared using this base oil are shown in the following table, which gives a summary of the oil compositions and Lauson engine test results:

Example No.	Lubricating oil Composition	Lauson engine test results			
		Detergency at 60 hrs., percent	Bearing weight loss, mgs., at—		
			20 hrs.	40 hrs.	60 hrs.
VI	Base oil—No additive.	58	200	400	(¹)
IV	Base oil+calcium sulfonate, 0.22% SO ₄ ash.	82	250	590	(¹)
V	Base oil+Ca salt of octyl phenol-formaldehyde resin, basic catalyst, thinner solution, 0.31% SO ₄ ash.	48	4	12	137
VIII	Base oil+Ca salt of octyl phenol-formaldehyde resin, basic catalyst, oil solution, 0.31% SO ₄ ash.	52	6	18	130
VII	Base oil+Ca salt of octyl phenol-formaldehyde resin, HCl catalyst, oil solution, 0.31% SO ₄ ash.	67	2	85	218
III	Base oil+Ca salt of octyl phenol-formaldehyde resin, 0.31% SO ₄ ash, basic catalyst, thinner+calcium sulfonate, 0.22% SO ₄ ash.	88	21	165	396
I	Base oil+Ca salt of modified octyl phenol-formaldehyde resin, thinner solution, 0.53% SO ₄ ash (0.22% from sulfonate and 0.31% phenol salt).	96	9	19	54
	Base oil+Ca salt of modified octyl phenol-formaldehyde resin, oil solution, 0.6% SO ₄ ash (0.11% from sulfonate, 0.49% phenol salt).	94	2	12	45

¹ Because of excessive corrosion the copper-lead bearings were replaced with babbitt bearings at the 40-hour examination.

Example X

A modified phenol-aldehyde resin is prepared by heating a mixture of 500 g. (3.05 equivalents) of tert. amyl phenol, 1,000 g. of an oil solution of sulfonic acids containing about 62% acids (1.35 equivalents) prepared from commercial calcium sulfonate according to the method described in Example I and 2,000 g. of an SAE 10 solvent treated Western mineral lubricating oil having a viscosity index of 90. This mixture is heated with vigorous stirring to 180° F. and 300 ml. of 40% formalin solution is added slowly. The resulting mixture is heated at a temperature between 180° and 210° F. for 3 hours and, with continued stirring, an amount of strontium hydroxide substantially equivalent to the phenol and sulfonic acid employed in the preparation of the mixture is added along with 100 ml. of water. The mixture is heated to about 375° F. to expel the water and filtered. This product has a sulfate ash of 9.8%, of which about 3.3% is due to the strontium salt of the sulfonic acid portion of the resin and about 6.5% is due to the calcium salt of the phenolic materials present in the resin.

A lubricating oil is prepared by dissolving the above oil concentrate in a naphthenic mineral lubricating oil having a viscosity index of 50 in

an amount to give an oil containing 1.5% sulfate ash. This oil has a detergency of 97% and a bearing weight loss at 60 hours of 50 mgs.

Example XI

Example X is repeated employing freshly precipitated tin hydroxide in place of the strontium hydroxide. The resulting product, which consists of the tin salt of the modified phenol-aldehyde condensation product, is dissolved in mineral lubricating oil in the ratio of 20 parts of the oil concentrate of the additive salt to 80 parts of lubricating oil. This oil has a detergency rating greater than 94 and a bearing weight loss at 60 hours of less than 75 in the Lauson engine test.

Example XII

Example X is repeated employing an equivalent amount of acetaldehyde and water in place of formalin. The resulting product is similar to the one obtained with formaldehyde.

Example XIII

Example X is repeated employing freshly precipitated zinc hydroxide in place of the strontium hydroxide. The resulting product, which consists of the zinc salt of the modified phenol-aldehyde condensation product, when dissolved

in mineral lubricating oil imparts the desirable detergency and anticorrosion characteristics to the oil.

Example XIV

Example X is repeated employing the equivalent amount of lead oxide in place of the strontium hydroxide. In this case, the product consists of the lead salt of the modified phenol-aldehyde condensation product. This product is dissolved in mineral lubricating oil in the ratio of 15 parts of the lead salt concentrate in oil and 85 parts of oil. This oil has a detergency rating of 95 and a bearing weight loss at 60 hours of less than 70 in the Lauson engine test.

Example XV

A modified phenol-aldehyde resin is prepared by heating a mixture of 300 g. (1.83 equivalents) of tert. amyl phenol, 1,000 g. of a sulfonic acid concentrate in oil containing about 62% of sulfonic acid (1.35 equivalents) and being prepared from commercial calcium sulfonate according to the method described in Example I, and 2,000 g. of an SAE 10 solvent treated Western mineral lubricating oil of 90 V. I. This mixture is heated with vigorous stirring to 175° F. and 180 ml. of 40% formalin solution is added slowly to the mixture. Heating is continued for about 3 hours at

200° F. and the resulting product is neutralized with sodium hydroxide added as an aqueous solution. Water is removed by heating to 350° F. and the product filtered.

A lubricating oil prepared by dissolving the above oil concentrate of the sodium salt in a 95 V. I. mineral lubricating oil in the ratio of 10 parts of the oil concentrate to 90 parts of oil has good detergency and anticorrosion characteristics.

Example XVI

A mixture of 200 g. of octyl phenol (0.97 mol), 2,000 g. of a light paraffinic mineral lubricating oil and 2,000 g. of an oil concentrate of sulfonic acids containing about 62% of sulfonic acids (approximately 2.7 moles) is heated to 100° F. To this mixture is added 58.4 g. (1.95 moles) of polymethylene oxide and 50 ml. of water and the mixture is heated with stirring to a temperature of about 200° F. for 3 hours. To the heated mixture is added 400 g. (3.6 equivalents) of lead oxide, which is the amount of lead oxide required to react with the acid product of condensation. Heating is continued for 6 hours, during which time the temperature is gradually increased to about 300° F. and the product is then filtered. The resulting product is the lead salt of the modified phenol-aldehyde resin. The product contains about 8% by weight of lead, of which about 6% corresponds to the lead salt of the sulfonic acids used in the preparation of the modified complex and 2% corresponds to the lead salt of the phenolic portion of the condensation product.

A lubricating oil is prepared by dissolving 10 parts of the oil concentrate of the above lead salt in 90 parts by weight of an SAE 30 paraffinic mineral lubricating oil. This product has a detergency rating greater than 95 in the Lauson engine and a bearing weight loss of 80 mgs. at 60 hours.

A second mineral lubricating oil is prepared in which 30 parts of the oil concentrate of the lead salt is dissolved in 70 parts of the same SAE 30 mineral lubricating oil. This product has a detergency greater than 98 and a bearing weight loss less than 50 mgs. at 60 hours.

Example XVII

A mixture of 200 g. (0.97 mol) of octyl phenol, 2000 g. of an SAE 10 paraffinic lubricating oil and 2000 g. (approximately 2.7 moles) of an oil concentrate of mahogany sulfonic acids containing about 62% by weight of sulfonic acids is heated to 90° F. To this mixture is added 120 ml. of 40% by volume formalin solution. The formalin is added drop-wise over a period of about 15 minutes while maintaining a temperature between 90° F. and 100° F. and the temperature is then raised to 200° F. for 3 hours. The resulting acid product is neutralized with a quantity of aqueous sodium hydroxide equivalent to the acid content of the modified resin, the product heated to 300° F. to eliminate water and subsequently filtered.

A lubricating oil is prepared by dissolving 10 parts by weight of the above sodium salt concentrate in oil in 90 parts by weight of an SAE 30 paraffinic mineral lubricating oil. This oil has the desired detergency and anticorrosion characteristics.

The foregoing description and examples of my invention are not to be taken as limiting since many 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 lubricating oil additive adapted to be diluted with mineral lubricating oil to produce a lubricating oil having detergent and anti-corrosion characteristics, said additive comprising a solution of mineral lubricating oil and an oil-soluble metal salt of the acidic reaction product obtained by condensing, in mineral lubricating oil solution, a mixture of petroleum sulfonic acids and a hydrocarbon substituted phenol having at least 1 hydrocarbon substituent of at least 3 carbon atoms, in which the ratio of mols of sulfonic acids to mols of phenol is between about 0.05 and 3 to 1, and which solution contains a volume of oil at least equal to the volume of sulfonic acids present, with between about 1.25 and 2 equivalents of a low molecular weight aldehyde containing from 1 to 5 carbon atoms per molecule, said condensing being effected by heating to a temperature between 150° F. and 300° F.

2. A composition according to claim 1 in which said oil-soluble metal salt is a polyvalent metal salt.

3. A composition according to claim 1 in which said oil-soluble metal salt is an alkaline earth metal salt.

4. A composition according to claim 1 in which said oil-soluble metal salt is a calcium salt.

5. A composition according to claim 1 in which said oil-soluble metal salt is a lead salt.

6. A composition according to claim 1 in which said low molecular weight aldehyde is formaldehyde.

7. A mineral lubricating oil containing a minor but effective proportion, sufficient to impart detergency and anti-corrosion characteristics to said oil, of an oil-soluble metal salt of the acidic reaction product obtained by condensing a mixture of petroleum sulfonic acids and a hydrocarbon substituted phenol having at least 1 hydrocarbon substituent of at least 3 carbon atoms, in which the ratio of mols of sulfonic acids to mols of phenol is between about 0.05 and 3 to 1 with between about 1.25 and 2 equivalents of a low molecular weight aldehyde containing from 1 to 5 carbon atoms per molecule, said condensing being effected by heating to a temperature between 150° F. and 300° F.

8. A mineral lubricating oil comprising mineral lubricating oil containing between about 0.5% and 20% of an oil-soluble metal salt of the acidic reaction product obtained by condensing a mixture of petroleum sulfonic acids and a hydrocarbon substituted phenol having at least 1 hydrocarbon substituent of at least 3 carbon atoms, in which the ratio of mols of sulfonic acids to mols of phenol is between about 0.05 and 3 to 1 with between about 1.25 and 2 equivalents of a low molecular weight aldehyde containing from 1 to 5 carbon atoms per molecule, said condensing being effected by heating to a temperature between 150° F. and 300° F.

9. A mineral lubricating oil according to claim 8 in which said lower molecular weight aldehyde is formaldehyde.

10. A mineral lubricating oil according to claim 8 in which said oil-soluble metal salt is a polyvalent metal salt.

11. A mineral lubricating oil according to claim 8 in which said oil-soluble metal salt is an alkaline earth metal salt.

12. A mineral lubricating oil according to claim 8 in which said oil-soluble metal salt is a lead salt.

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13. A mineral lubricating oil according to claim 8 in which said oil-soluble metal salt is a zinc salt.

14. A mineral lubricating oil according to claim 8 in which the amount of oil-soluble metal salt incorporated in said oil is sufficient to impart a sulfate ash content to said oil of between about 0.1% and 6%.

15. A mineral lubricating oil according to claim 8 in which said sulfonic acids are mahogany sulfonic acids.

16. A mineral lubricating oil according to claim 8 in which said oil-soluble metal salt is an alkali metal salt.

17. A mineral lubricating oil comprising mineral lubricating oil containing between 0.5% and 20% by weight of an oil-soluble metal salt of the acidic reaction product obtained by heating a mixture of petroleum sulfonic acids and a hydrocarbon substituted phenol having at least 1 hydrocarbon substituent of at least 3 carbon atoms to a temperature between 175° F. and 220° F., adding thereto between 1.25 and 2 equivalents per equivalent of phenol of a low molecular weight aldehyde having 1 to 5 carbon atoms per molecule and heating the resulting mixture to a temperature between 225° F. and 300° F. to effect condensation.

18. A mineral lubricating oil consisting of a mineral lubricating oil containing between about 0.5% and 20% by weight of an oil-soluble metal salt of the acidic reaction product obtained by

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heating, to a temperature within the range of 150° F. to 300° F. to effect condensation, a mixture of 1.25 to 2 equivalents of a low molecular weight aldehyde having 1 to 5 carbon atoms per molecule, 0.05 to 3 mols of petroleum sulfonic acids and 1 mol of a hydrocarbon substituted phenol having at least 1 hydrocarbon substituent of at least 3 carbon atoms together with a small amount of water.

LOREN L. NEFF.

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