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LUBRICATING OIL CONTAINING A METAL
SALT OF A CONDENSATION PRODUCT OF
AN ALKYL SUBSTITUTED PHENOL AND
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Calif., a corporation of CaliforniaNo Drawing. Application July 17, 1950,
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This invention relates to lubricating oil addition agents having exceptional anti-corrosion and detergent characteristics when added to mineral lubricating oil, and to lubricating oils containing such addition agents with and without supplemental detergents. More particularly, the invention relates to oil-soluble metal salts of the condensation products obtained by condensing hydrocarbon substituted phenols with olefin oxides as will be described herein and to lubricating oils containing such metal salts.

The present trend in internal combustion engines, particularly of the diesel engine type, is in the direction of higher compression ratios, higher operating temperatures and thus higher horse power output per unit weight of the engine. Moreover, it is the trend to operate engines of this type for longer periods without oil change so that oils which are satisfactory for use in the present-day high output diesel engines, for example, must have not only an initially high detergency and initially high anti-corrosion characteristics but these properties must be retained under severe conditions of use for relatively long periods of use in an engine. To further complicate the preparation of a satisfactory oil for the lubrication of such engines the fuels available often contain higher proportions of sulfur than those which have been used in the past and it is well recognized that high sulfur fuels tend to produce corrosive conditions in an engine which must be overcome by the lubricating oil employed, otherwise not only does corrosion take place in the engine but wear rates are sufficiently high that frequent overhaul and replacement of parts becomes necessary, thereby unduly increasing engine operation cost.

It is an object of this invention to prepare lubricating oils which will operate satisfactorily in internal combustion engines and particularly in the high output diesel engines over relatively long periods of service. It is another object to prepare such lubricating oils which will protect engines of this type operating under severe conditions even while using a fuel containing as high as 1% or more of sulfur.

It is found that these and other objects can be obtained by adding to mineral lubricating oil relatively small amounts of an oil-soluble metal salt of the condensation product of a hydrocarbon substituted phenol and an olefin oxide as defined hereinbelow.

Thus the invention resides in lubricating oils containing between about 0.05% and about 10% or as high as about 20% by weight of an oil-sol-

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uble metal salt of the condensation product obtained by condensing a hydrocarbon substituted phenol wherein the hydrocarbon substituent or substituents contain between about 4 and about 30 carbon atoms with a low molecular weight olefin oxide which may also be described as an epoxyalkane. These condensation products are acidic and capable of reacting with metal bases, as for example, metal oxides, hydroxides and carbonates, under appropriate conditions to form the corresponding metal salts.

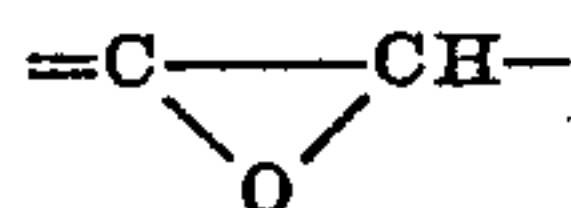
Typical oil-soluble metal salts are produced by reacting approximately one molecular proportion of a hydrocarbon substituted phenol such as octylphenol with one molecular proportion of ethylene oxide or propylene oxide. In the case of propylene oxide, the phenol and oxide are dissolved in about 2 parts by volume of a petroleum naphtha and to the solution is added about 2 parts by volume of a condensation catalyst or agent, e. g. sulfuric acid. The catalyst is added slowly and the temperature of the reaction mixture is maintained at about 20° C. to 30° C. at which temperature the reaction is found to be complete in about 3 hours. Since the reaction is exothermic cooling is necessary in order to maintain the temperature within the desired range. Following the completion of the reaction the product is water washed until free of mineral acid. Upon evaporation of the solvent naphtha employed there remains a resinous material having a dark brownish color. The resin may be converted into its metal salt, as for example the barium salt, by treatment of a solvent solution, as for example a naphtha or a hydrocarbon lubricating oil solution, of the resin with barium hydroxide octahydrate or with anhydrous barium hydroxide, in which latter case it is necessary to add small amounts of water during the neutralization. Where the metal salt is the desired product, a thinner or naphtha solution of the condensation product is mixed with the desired metal base and, after neutralization and elimination of water, the solvent is evaporated leaving the metal salt of the condensation product. The barium salt of the above condensation product is a semi-solid to solid resin of brownish color. Where it is desirable to prepare a lubricating oil concentrate of the metal salt of the condensation product the neutralization is preferably effected in mineral oil solution. In this case the condensation product or the solvent solution of the condensation product is dissolved in about 1 to about 5 volumes of mineral lubricating oil and the desired metal base and water is added. The re-

sulting product is agitated and heated sufficiently to effect complete neutralization and subsequently filtered to remove solid impurities. The resulting product will be referred to as an oil concentrate of an oil-soluble metal salt of the condensation product of a hydrocarbon substituted phenol and an olefin oxide.

Hydrocarbon substituted phenols which are useful in the preparation of the oil-soluble metal salts of this invention include the phenols having alkyl, cycloalkyl, aryl, aralkyl and alkaryl substituents. The substituents may be in the ortho-, meta- or para- positions. Preferably the compound will have either an ortho- and a para-position free of substituents, or if the para-position is substituted then preferably both ortho-positions should be free of substituents. Alkyl substituents include the butyl, amyl, isoamyl, hexyl, heptyl, octyl, lauryl, cetyl and like radicals. These radicals may be normal or branched chain groups and the phenol may contain one or more of these substituents. Moreover, the alkyl substituents include the so-called wax radicals, i. e. radicals derived from paraffin wax which may contain as high as 30 or more carbon atoms. Wax phenols are well known in the art and may be prepared by reacting phenol with chlorinated paraffin wax in the presence of a Friedel-Crafts catalyst. Cycloalkyl substituents include cyclohexyl, methylcyclohexyl, cyclopentyl, methyl, ethyl and propyl cyclopentyl radicals and the like. Aryl radicals include the phenyl radical, as for example phenylphenol. Aralkyl radicals include the benzyl radical and thus benzylphenol. Alkaryl radicals include the radicals such as methylphenyl, ethylphenyl and the like.

Olefin oxides are described and their method of preparation is given in *The Petroleum Chemicals Industry* by R. F. Goldstein, E. and F. N. Spon Ltd., London, 1949, page 349 et seq. These compounds are prepared by treating olefins with aqueous solutions of chlorine to yield the corresponding chlorhydrins. The chlorhydrin is then treated with caustic alkali to form the olefin oxide. Preferably the olefin oxide is removed as it is formed to prevent hydrolysis to the glycol.

Compounds to be included within the terms "olefin oxides," "low molecular weight olefin oxides" or "epoxyalkanes" as used herein are those compounds containing the group



where the remaining valences of the carbon atoms are satisfied with hydrogen and/or alkyl groups. The alkyl groups may be normal or branched chain. Since it is found that the ability of these olefin oxides to form condensation products decreases with increasing molecular weight it is only the lower molecular weight olefin oxides, i. e., those containing up to about 8 carbon atoms, which appear to have sufficient reactivity in the condensation reaction to have utility in accordance with the invention. Thus the total carbon atom content of the alkyl radicals in the above formula will be between 0, as in ethylene oxide, and about 6.

Preferably the olefin oxides to be employed will be those containing the group



where the remaining valence of carbon is satisfied with hydrogen or with an alkyl group containing between 1 and about 6 carbon atoms and

of this group of compounds, ethylene oxide and 1,2-propylene oxide are particularly preferred. Since in this preferred group of olefin oxides the oxygen atom is attached to the terminal carbon atom and the adjacent carbon atom, these compounds are generally referred to as 1,2-olefin oxides or 1,2-epoxyalkanes.

Within the preferred group of olefin oxides, in addition to ethylene oxide and propylene oxide mentioned, are butylene oxide (1,2-epoxybutane), 1,2-epoxypentane, 1,2-epoxy-3-methylbutane, the 1,2-epoxyhexanes, e. g. 1,2-epoxy-3-methylpentane and the various isomeric 1,2-epoxyheptanes and octanes. These compounds as well as the corresponding compounds where the oxygen atom is in the 2,3- position or the 3,4- position in the case of epoxyoctane, and compounds such as 1,2-epoxyisobutane and other compounds having two alkyl radicals attached to one of the carbon atoms which is in turn attached to oxygen are included in the broader group of olefin oxides which fall within the scope of this invention. Thus 2,3-epoxybutane, 2,3-epoxypentane and the like have utility and are to be considered as olefin oxides which react with hydrocarbon substituted phenols to form condensation products as defined herein.

The molar ratio of hydrocarbon substituted phenol to olefin oxide compound to be used in preparing desirable condensation products will be between about 0.5 and about 3 to 1. Preferably this molar ratio will fall between about 0.8 and about 2 to 1. Particularly satisfactory results have been obtained using approximately equal molecular proportions of phenol and olefin oxide.

Catalysts or condensation agents which may be employed and which serve to effect the desired condensation reaction include the acid catalysts, as for example sulfuric acid and phosphoric acid, as well as the Friedel-Crafts type catalysts including aluminum chloride, boron trifluoride, zinc chloride and the like. In the case of boron trifluoride, this compound is generally employed in the form of its complex with diethyl ether. The complex is known as boron trifluoride etherate and has a boiling point of about 125° C. The amount of catalyst to be employed will generally be between about 0.5% and 10% by weight of the total reactants. However, as much as 20% may be employed if desired, with satisfactory results.

Although the condensation reaction will take place in the absence of solvent or diluent, it is generally desirable to employ a solvent during the condensation reaction. Solvents which may be employed include those which do not react with phenols or with the olefin oxides under the conditions of condensation. Such solvents include the hydrocarbon naphthas or thinners, aromatic solvents, as for example benzene, toluene, and xylene, and the like as well as chlorinated solvents such as chloroform, carbon tetrachloride and the like. Also, the condensation is satisfactorily effected using mineral oil as the solvent or diluent. Thus, the solvent can be the oil to be used in the preparation of the final lubricating oil composition. The amount of solvent or diluent to be employed may be widely varied, although generally between 0.5 and 5 volumes of solvent per volume of reactants is found to give satisfactory results.

The temperature of reaction will depend upon the reactants involved but will generally be between about -20° C. and about 200° C. and pref-

erably between about 0° C. and about 100° C. or 150° C. The temperature employed will depend to some extent upon the volatility of the allyl compound employed and also upon the reactivity of the olefin oxide. With the more volatile compounds, as for example ethylene oxide, lower temperatures are generally preferred and pressures up to 3 or 4 atmospheres may be employed if desired in order to maintain the reactants in solution or in liquid condition at the temperatures employed, or preferably the ethylene oxide is bubbled into a solution of the phenol and condensation agent.

The time of reaction is dependent upon the particular reactants and upon the temperature and condensation agent employed, although generally it is found that between about 1 hour and 8 or 10 hours suffices to effect the desired extent of condensation. However, entirely satisfactory condensation products have been prepared when the reaction conditions were maintained for as long as 24 hours. Products so obtained are found to be oil-soluble and metal salts derived from the condensation products are also oil-soluble. It is to be noted that with the higher molecular weight olefin oxides as much as 20-25 hours is sometimes necessary where it is desired to carry the condensation to completion. Moreover, in the case of olefin oxides having two alkyl groups attached to one of the carbons of the epoxy group it is usually desirable to carry out the reaction at low temperatures, e. g. 0° C. to 20° C. in order to avoid side reactions which tend to occur at elevated temperatures. Just what these reactions are is not known, however it is found that with 1,2-epoxyisobutane, for example, a better condensation product is obtained and more of the phenol is reacted at these low temperatures than when the temperature is permitted to rise above about 25° C. or 30° C.

The metals to be employed in preparing metal salts of the condensation products are preferably the polyvalent metals, although the monovalent alkali metals are satisfactory in some instances. Thus the sodium, potassium and lithium salts are found to be oil-soluble and have the desired characteristics when added to mineral lubricating oils. Of the polyvalent metals, the alkaline earth metals calcium, magnesium, barium and strontium are particularly effective. However, the zinc, lead and aluminum salts are suitable and in some cases chromium, iron, nickel, cobalt, mercury, tin and other polyvalent metal salts have utility and are to be considered part of this invention, although this latter group of polyvalent metal salts are not to be considered equivalent to the alkali and alkaline earth metals and zinc, lead and aluminum salts.

In preparing metal salts of the acidic condensation products a solvent solution or a lubricating oil solution of the condensation product is heated with the desired metal base, i. e. oxide, hydroxide or carbonate, in the presence of a small amount of water or in the presence of a small amount of alcohol. The mixture is agitated and heated to eliminate water and/or alcohol and effect neutralization. In the case of the more weakly basic metals the metal salt is preferably made by a method involving first preparing the alkali metal salt, as for example the sodium salt, and subsequently metathesizing the alkali metal salt with an inorganic salt of the desired metal. This metathesis is carried out in alcoholic solution in order to prevent hydrolysis which would occur in aqueous solution.

Methods of metathesizing weak acid salts are well known in the art and therefore need no further description here. This same method of preparation may be employed in producing any of the polyvalent metal salts if so desired.

In preparing finished lubricating oils the oil-soluble metal salts or the oil concentrates thereof, produced as indicated above, are added to mineral lubricating oil in proportions such that the final oil will contain between about 0.05% and about 20% and preferably between about 0.5% and 10% by weight of the metal salt. Although no difficulty is encountered in preparing oil solution because of the ready oil-solubility or oil-dispersibility of these compounds, the solutions are generally prepared by heating the oil containing the metal salt to a temperature of 100° C. to 150° C. and agitating the solution to effect rapid and complete solution and/or dispersion. Lubricating oils which may be employed include substantially all types of mineral lubricating oils. Thus the oil may be one having a viscosity index of 0 or even lower or it may be a paraffinic type oil having a viscosity index in the neighborhood of 100. Particularly satisfactory results have been obtained using a solvent treated Western paraffinic mineral lubricating oil having a viscosity index of between about 85 and 95.

Although lubricating oils containing the additive of this invention as the only additive material are particularly effective, it is often desirable, particularly where the oil is to be used under severe service conditions, to incorporate in the oil relatively small amounts, as for example 0.5% to 8 or 10% by weight, of a supplemental detergent. It is found, for example, that oil-soluble metal sulfonates and particularly the oil-soluble metal salts of mahogany sulfonic acids obtained by treating lubricating oil fractions of petroleum with sulfuric acid, SO₃ or chlorosulfonic acid, which methods of preparation are well known in the art, appear to cooperate with the additives of this invention to produce outstanding lubricating oils. Thus by adding between about 0.5 and 5% by weight of a metal petroleum sulfonate it is found that the detergency of the oil is improved without adversely affecting the anti-corrosion or anti-oxidation characteristics of the oil.

Another detergent which appears to cooperate with the additives of this invention is a modified sulfonate prepared by heating an oil-soluble metal petroleum sulfonate with an inorganic base to solubilize the base in the sulfonate. Thus, mahogany sulfonic acids may be reacted with inorganic bases as, for example, with metal oxides, hydroxides, carbonates and bicarbonates, to produce oil-soluble complexes containing a ratio of equivalents of metal to sulfonic acids between 1.1 to 1 and 3 or more to 1 and these materials are found to impart exceptional detergency characteristics to lubricating oils containing the condensation product salts of this invention. Such oil-soluble complexes of sulfonic acids and metal hydroxides, oxides, carbonates and the like which may be employed together with the additive of this invention are those described by Mertes in U. S. Patents Nos. 2,501,731 and 2,501,732.

The metals to be employed as constituents of the sulfonate or modified sulfonate supplemental detergents are the same as those described hereinabove as being useful as constituents of the condensation products.

The evaluation of lubricating oils containing

the oil-soluble metal salts of this invention has been carried out in Lauson single cylinder engines. Tests in the Lauson single cylinder test engines are carried out 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 horse power, 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 babbitt 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.

The following examples illustrate some modifications of the invention, however it is to be realized that various modifications of the described methods of preparation and the described condensation product salts come within the scope of the invention.

Example I

A mixture of 206 g. of octylphenol and 67.6 ml. of propylene oxide is cooled to 20° C. and 54 ml. of concentrated sulfuric acid is added dropwise to the mixture. The temperature rises rapidly to approximately 80° C. during the addition of the initial 9 ml. of acid. At this point the mixture is cooled to 20° C. and 500 ml. of a light paraffinic naphtha is added. The remainder of the sulfuric acid is added slowly and the temperature maintained as nearly as possible at about 20° C. Following the addition of acid, which requires about 45 minutes, the mixture is stirred for an additional hour at room temperature and then water washed to remove free mineral acid. The product is topped to 150° C. to remove naphtha, leaving a brown semi-solid resin as a residue.

The barium salt of this resin is prepared by adding 28 g. of anhydrous barium hydroxide and 100 ml. of water (the water being added dropwise) to a solution of 75 g. of the resin in 925 g. of an SAE 30 solvent treated western paraffinic mineral lubricating oil having a viscosity index of about 87 and a pour point of -30° C. The mixture is heated to 175° C. and filtered hot through filter aid to obtain as filtrate an oil concentrate of the barium salt of octylphenol-propylene oxide condensation product.

A lubricating oil is prepared by dissolving 12% by weight of the above oil concentrate in mineral lubricating oil of the type described above. This oil has a viscosity index of 84 and a pour point of -5° C. and when tested in a Lauson engine has

a detergency over 95% and a bearing weight loss at 60 hours of less than 350 mg.

Example II

A 412 g. portion of p-octylphenol is dissolved in one liter of a light petroleum naphtha consisting primarily of hexanes and heptanes and having a boiling range of 60°-100° C. Gaseous ethylene oxide is bubbled into the solution and 27 ml. of concentrated sulfuric acid is added dropwise through a reflux condenser. The rate of addition of ethylene oxide is regulated so that approximately 2 mols is added during the addition of the acid. The temperature increases to reflux temperature (72° C.) within a short time and the rate of sulfuric acid addition is so regulated that excessive boiling does not occur. Following the addition of all of the acid and approximately 2 mols of ethylene oxide the reaction mixture is refluxed for one hour and then water washed to remove free mineral acid.

Approximately one-half of the water-washed product is dissolved in 1000 g. of the mineral lubricating oil described Example I and 173 g. of barium hydroxide octahydrate is added. The mixture is heated gradually to 175° C. with stirring and filtered hot to obtain as filtrate an oil concentrate of the barium salt of an octylphenol-ethylene oxide condensation product.

The remaining one-half of the water-washed material above described is treated with 46 g. of lithium hydroxide monohydrate and 10 ml. of water. The mixture is refluxed for 2 hours and the refluxing then continued with a water trap in the reflux line until no further water is obtained in the trap. The mixture is cooled, filtered and topped to about 150° C. to remove naphtha. The product is the lithium salt of octylphenol-ethylene oxide condensation product.

Lubricating oils prepared with each of the metal salts above described are found to have good detergency and anti-corrosion characteristics.

Example III

Ethylene oxide is bubbled through a mixture of 220 g. of nonylphenol and 25 ml. of boron trifluoride etherate. The temperature of the reaction mixture is maintained at about 30° C. during the blowing with ethylene oxide until approximately 33 g. of the oxide has been used. The mixture is then stirred for 2 hours at about 30° C., diluted with one liter of naphtha and water washed until free of mineral acid.

The product is dissolved in 1750 g. of lubricating oil of the type described in Example I and to the solution is added 41 g. of calcium hydroxide and 50 ml. of water. The mixture is heated gradually to 175° C. and filtered hot through filter aid to obtain as filtrate an oil concentrate of the calcium salt of nonylphenol-ethylene oxide condensation product.

A lubricating oil containing 8% by weight of the above oil concentrate in lubricating oil of the type used in preparing the concentrate is found to operate satisfactorily in a Lauson test engine.

Example IV

To a solution of 529 g. of cyclohexylphenol and 210 ml. of propylene oxide in 3 liters of light petroleum naphtha is added 82 ml. of concentrated sulfuric acid. The acid is added slowly while maintaining the temperature at about 25° C. When the addition of acid is complete the mixture is stirred for an additional 3 hours at

about 25° C. and then washed with water to remove mineral acid. The water-washed product is dissolved in 3500 g. of SAE 30 mineral lubricating oil of the type described in Example I and the solution heated to 150° F. to evaporate the naphtha.

To approximately one-third of the oil-solution of the condensation product is added 123 g. of lead oxide (PbO) and 75 ml. of water. The mixture is heated gradually to 175° C. and filtered hot through filter aid to obtain an oil concentrate of the lead salt of cyclohexylphenol-propylene oxide condensation product.

The remaining two-thirds of the topped oil solution of concentrate is treated with 88 g. of sodium hydroxide in the form of a 45 weight percent aqueous solution. The mixture is heated to 200° C. and filtered hot to obtain as filtrate an oil solution of the sodium salt of cyclohexylphenol-propylene oxide condensation product.

Approximately one-half of the concentrate of sodium salt prepared as described in the preceding paragraph is dissolved in 2 liters of naphtha and a solution of 75 g. of anhydrous zinc chloride in 500 ml. of isopropanol is added. The mixture is stirred vigorously for 3 hours and then heated to 175° C. The resulting product is filtered to obtain as filtrate an oil concentrate of the zinc salt of cyclohexylphenol-propylene oxide condensation product.

Lubricating oils are prepared from each of the above metal salts. In each case sufficient of the metal salt concentrate is employed to produce a lubricating oil containing 4% by weight of the metal salt. The oil employed is an SAE 30 naphthenic lubricating oils having a viscosity index of about 50. Each of the three oils operates satisfactorily in Lauson test engines and has high detergency and good anti-corrosion characteristics.

Example V

The equivalent amount of isobutylene oxide is substituted for propylene oxide in the above example and the condensation reaction is carried out at a temperature of approximately 20° C. Lubricating oils containing the lead, sodium and zinc salts of the cyclohexylphenol-isobutylene oxide condensation product in the amounts indicated in the preceding example have high detergency and good anti-corrosion characteristics.

Example VI

A 170 g. portion of p-phenylphenol and 25 ml. of boron trifluoride etherate are dissolved in 1500 ml. of a light petroleum naphtha. To this solution 70 ml. of propylene oxide is added slowly with stirring while maintaining the temperature of the reaction mixture at about 30° C. When all of the propylene oxide is added the temperature is raised to about 80° C. where refluxing occurs and the mixture is refluxed for 2 hours. The reaction product is washed free of mineral acid using water.

The water-washed naphtha solution of condensation product is dissolved in 2000 g. of the mineral lubricating oil described in Example I and to the solution is added 32 g. of freshly precipitated magnesium hydroxide and 50 ml. of water. The resulting mixture is stirred and heated to 175° C. and filtered hot through filter aid. The resulting product is an oil concentrate of the magnesium salt of a phenylphenol-propylene oxide condensation product.

A lubricating oil prepared by dissolving 1000

g. of the above product in 5000 g. of mineral lubricating oil of the type used in preparing the concentrate has exceptional detergency and anti-corrosion characteristics as indicated by Lauson engine tests.

Example VII

Example VI is repeated using an equivalent amount of 1,2-epoxyhexane in place of propylene oxide. The epoxyhexane is prepared by treating hexene-1 with hypochlorous acid to form the chlorhydrin and reacting chlorhydrin with sodium hydroxide according to methods well known in the art. The condensation reaction is carried out at a temperature of about 50° C. and following the addition of the 1,2-epoxyhexane the temperature is raised to 80° C. and the mixture refluxed for 10 hours.

A magnesium salt of the condensation product prepared as indicated in the preceding example is found to impart detergency and anti-corrosion characteristics to mineral lubricating oil.

Example VIII

A 610 g. portion of pentadecylphenol is dissolved in 5000 g. of an SAE 10 solvent refined paraffinic Western mineral lubricating oil having a viscosity index of about 85 and 54 ml. of concentrated sulfuric acid is added to the mixture. The mixture is stirred and while being maintained at about 25° C. ethylene oxide is bubbled through the reaction mixture until a total of approximately 44 g. of ethylene oxide has been absorbed. The mixture is then washed free of mineral acid using hot water.

To the washed oil solution is added 123 g. of potassium hydroxide in the form of a 50 weight percent aqueous solution. The mixture is heated to 200° C. and filtered hot through filter aid to obtain as filtrate an oil concentrate of the potassium salt of pentadecylphenol-ethylene oxide condensation product.

To approximately one-half of the oil concentrate of potassium salt prepared as above is added 2 liters of naphtha and a solution of 143 g. of nickel chloride in 2 liters of isopropanol. The mixture is stirred vigorously for 3 hours and then heated to 175° C. to eliminate naphtha and isopropanol and then filtered. The product is an oil concentrate of the nickel salt of pentadecylphenol-ethylene oxide condensation product.

A lubricating oil prepared by dissolving 10% by weight of the above potassium salt concentrate in an SAE 30 mineral lubricating oil of the type described in Example I has a detergency greater than 90% in the Lauson engine test. This oil operates satisfactorily in such engine.

A second oil prepared by dissolving 15% by weight of the nickel salt concentrate in SAE 30 lubricating oil of the type used in Example I has a detergency greater than 94% in the Lauson engine test and a bearing weight loss at 60 hours of less than 350 mg.

Example IX

A paraffin wax having an average molecular weight of about 350 is treated with gaseous chlorine to obtain a chlorinated paraffin wax containing approximately one atom of chlorine per molecule of the wax. This product is condensed with phenol in the presence of anhydrous aluminum chloride to obtain a wax substituted phenol having a molecular weight of approximately 450.

A 450 g. portion of the above wax substituted phenol and 70 ml. of propylene oxide are dis-

solved in 2 liters of a light petroleum naphtha and to this solution is added 16 ml. of concentrated sulfuric acid. The acid is added slowly while maintaining a temperature in the reaction mixture of about 25° C. After the addition of acid is complete the mixture is refluxed at about 72° C. for 3 hours and then washed free of mineral acid with water.

The water-washed product is dissolved in 1500 g. of an SAE 30 mineral lubricating oil of the type described in Example I and to this oil solution is added 174 g. of barium hydroxide octahydrate. The mixture is stirred, heated to 175° C. and filtered hot through filter aid to obtain as filtrate an oil concentrate of the barium salt of a wax substituted phenol-propylene oxide condensation product.

A lubricating oil containing sufficient of the above concentrate to impart a barium salt content to the oil of 5% has a detergency greater than 94% and a bearing weight loss at 60 hours of less than 300 in the Lauson engine test.

A second lubricating oil containing the above proportion of barium salt and containing also 1.5% by weight of calcium petroleum sulfonate has a detergency in the Lauson engine test greater than 97% and a bearing weight loss of less than 325 in the Lauson engine test.

It is to be pointed out that the preceding examples are illustrative of the invention and are not to be considered as limiting because the phenols having one or more of the other hydrocarbon substituents described herein and other allyl compounds described herein are found to condense under similar conditions to form comparable condensation product. Moreover, the other metals described herein as being useful in preparing the metal salts of the condensation products may be substituted for the metals employed in the examples to give salts which are effective as detergents and anti-corrosion agents when added to mineral lubricating oils.

I claim:

1. A mineral lubricating oil containing between about 0.05% and about 20% by weight of an oil-soluble metal salt of the acidic reaction product obtained by condensing, in the presence of an acid condensation catalyst, at a temperature between about -20° C. and about 200° C., between 0.5 and 3 mols of a hydrocarbon substituted phenol in which the hydrocarbon substituent contains between about 4 and about 30 carbon atoms with 1 mol of a low molecular weight olefin oxide containing between 2 and about 8 carbon atoms per molecule.

2. A mineral lubricating oil according to claim 1 in which said olefin oxide is a 1,2-epoxy alkane.

3. A mineral lubricating oil according to claim 1 containing also between about 0.5% and about 10% by weight of an oil-soluble metal sulfonate.

4. A mineral lubricating oil according to claim 1 containing also between about 0.5% and about 10% by weight of a modified sulfonate obtained by heating an oil-soluble metal sulfonate with between about 0.1 and 2 equivalents of an inorganic metal base selected from the class consisting of metal oxides, hydroxides, carbonates and bicarbonates to solubilize said base in said sulfonate.

5. A mineral lubricating oil containing between about 0.5% and 10% by weight of an oil-soluble polyvalent metal salt of the acidic reaction product obtained by condensing an alkyl substituted phenol, in which the alkyl substituent contains between about 4 and about 30 car-

bon atoms, with an olefin oxide having between 2 and about 8 carbon atoms per molecule at a temperature between about 0° C. and about 100° C., the molar ratio of phenol to olefin oxide being between about 0.5 and 3 to 1.

6. A mineral lubricating oil according to claim 5 in which said polyvalent metal salt is an alkaline earth metal salt.

7. A mineral lubricating oil according to claim 5 in which said polyvalent metal salt is a barium salt.

8. A mineral lubricating oil according to claim 5 in which said hydrocarbon substituted phenol is p-octylphenol and said olefin oxide is ethylene oxide.

9. A mineral lubricating oil containing between about 0.5% and 10% by weight of an oil-soluble alkali metal salt of the acidic reaction product obtained by condensing, in the presence of an acid condensation catalyst, an alkyl substituted phenol, in which the alkyl substituent contains between about 4 and about 30 carbon atoms, with an olefin oxide having between 2 and about 8 carbon atoms per molecule at a temperature between about 0° C. and about 100° C. under a pressure sufficient to maintain the reactants in liquid condition, the molar ratio of phenol to olefin oxide being between about 0.5 and 3 to 1.

10. A mineral lubricating oil according to claim 9 in which said alkali metal salt is a lithium salt.

11. A mineral lubricating oil containing between about 0.05% and about 20% by weight of an oil-soluble metal salt of the acidic reaction product obtained by condensing, in the presence of a condensation catalyst selected from the class of condensation catalysts consisting of sulfuric acid, phosphoric acid, aluminum chloride, zinc chloride, boron trifluoride and boron trifluoride etherate, a hydrocarbon substituted phenol in which the hydrocarbon substituent contains between about 4 and about 30 carbon atoms with an olefin oxide containing between 2 and about 8 carbon atoms per molecule, the molar ratio of phenol to olefin oxide being between about 0.5 and 3 to 1.

12. A mineral lubricating oil containing between about 0.5 and about 10% by weight of an oil-soluble metal salt of the acidic reaction product obtained by condensing, in the presence of an acid condensation catalyst, approximately equal molecular proportions of an octylphenol and 1,2-propylene oxide in the presence of concentrated sulfuric acid as a condensation catalyst and at temperatures between about 20° C. and 80° C.

13. A mineral lubricating oil containing between about 0.5% and about 10% by weight of an alkaline earth metal salt of the acidic reaction product obtained by the condensing, in the presence of an acid condensation catalyst, approximately equal molecular proportions of nonylphenol and ethylene oxide in the presence of boron trifluoride etherate as a condensation catalyst at temperatures of about 30° C.

14. A lubricating oil according to claim 13 in which said alkaline earth metal is calcium.

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