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LUBRICATING COMPOSITION

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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 for 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 detergency 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 detergency additive is to be included in the composition than would be required if the detergency

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additive was 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 total 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 detergency, anticorrosion and anti-wear characteristics to the oil and it is a further object of this invention to prepare the additive material itself and to prepare oil concentrates of the additive material which may be readily incorporated in additional mineral oil to produce finished lubricants.

It is also an object of this invention to prepare an additive having exceptional anticorrosion and anti-wear characteristics which possesses at least some detergency characteristics, which additive may be used in conjunction with well known detergent additives, such as metal sulfonates particularly, to produce finished oils having exceptional detergency, anticorrosion and anti-wear characteristics.

It is found that these and other objects can be obtained by dissolving in mineral lubricating oils a small quantity, in the order of about 0.2% to about 10% or even 15% by weight, of oil-soluble metal salts of the condensation product of a hydrocarbon substituted phenol with acetylene.

In place of the metal salts, the oil-soluble condensation product itself may be dissolved in mineral lubricating oil in the same proportions to impart at least some of the desired anticorrosion, anti-wear and detergency characteristics to the oil. However, the oil-soluble metal salts are to be preferred particularly where detergency and anti-wear characteristics are important.

The condensation product referred to is the product obtained by reacting acetylene with a hydrocarbon substituted phenol under conditions which will be described hereinbelow to obtain a viscous liquid to solid resinous condensation and/or polymerization product. The preferred substituted phenol to be employed will be a phenol having a hydrocarbon substituent in the para position in which the hydrocarbon substituent is preferably an alkyl group but may be a cycloalkyl, aralkyl, alkaryl group having at least about 3 or 4 carbon atoms and generally less than about 30 or 35 carbon atoms. The substituent must be of sufficient carbon atom content to impart oil solubility to the resulting condensation product. Apparently 2 carbon atoms is insufficient for this purpose but 4 carbon atom groups and in some instances groups containing 3 carbon atoms are of sufficient size to impart oil solubility. Thus, butyl, isobutyl and tertiary butyl groups, as well as groups containing 5 or more carbon atoms give oil-soluble resins and under certain circumstances, particularly where liquid condensation products are obtained, the propyl and isopropyl phenols are useful. The condensation product is a weakly acidic non-carboxylic organic material due to its phenolic character, i. e. the presence of hydroxyl groups attached to the benzene nuclei. These condensation products are reacted with metal bases or basic metal compounds to form the corresponding metal salts or soaps, i. e. they may be reacted with hydrated lime, for example, to form the calcium salt, and it is the oil-soluble metal salts of the condensation products which constitute the preferred form of lubricating oil additives of this invention.

Although it is indicated that phenols having a single hydrocarbon substituent in the para position are the preferred phenolic compounds, phenols having hydrocarbon substituents in other positions, i. e. in the ortho or meta positions, may be successfully employed in the production of condensation products and salts thereof, which are useful in preparing the lubricating oils of this invention. Moreover, the phenolic compounds may contain more than one substituent and they may contain one or more hydroxyl groups. Thus, the term "hydrocarbon substituted phenol" as used herein will encompass cresols, xylenols, polyhydric phenols such as hydrocarbon substituted resorcinols and the like. Moreover, condensed ring aromatic compounds having hydroxyl groups attached to one or more of the rings, such as hydrocarbon substituted naphthols and like, may be employed. When the phenol contains more than one substituent group the total carbon atom content of the substituents must be sufficient to impart oil solubility to the resulting condensation products and apparently at least about 4 carbon atoms are necessary and a total carbon atom content of less than 30 or 35 is desirable. Hydrocarbon substituents referred to are any of the above mentioned hydrocarbon groups suitable in the case of para substituted phenols.

The invention therefore resides in metal salts of the condensation products of hydrocarbon substituted phenols with acetylene, in mineral lubricating oils containing such metal salts in the proportion of about 0.5% to as much as 15% by weight in mineral oils containing the condensation products per se in the same proportions and in mineral oils containing such condensation products and/or metal salts thereof with or without the addition of detergent additives with which said condensation products or metal salts thereof cooperate to produce exceptional lubricating oils. The invention resides also in lubricating oils containing 15% or 20% to 70% or 80% of the salts or condensation products, which concentrated solutions will be referred to as concentrates.

In its preferred form the invention resides in mineral lubricating oils containing between about 0.5% and about 10% by weight of metal salts of the condensation products obtained by condensing hydrocarbon substituted phenols with acetylene since apparently the metal salts impart greater detergency, better protection against corrosion and greater wear resistance to mineral lubricating oils than do the condensation products themselves. This increased protection is at least in part connected with the ability of the salts to react with corrosive acids formed in the lubricating oils during use whereby non-corrosive metal salts, for example calcium salts of the corrosive acids, are formed and the weakly acidic non-corrosive phenolic condensation compounds are released. The released phenolic condensation products still serve as anticorrosion agents in the oil as would be indicated by the fact that such materials alone impart anticorrosion characteristics to an oil. The salts impart to the oil what may be termed "reserve alkalinity" because of their ability to neutralize strong corrosive acids. It is believed that the condensation products themselves, and particularly the metal salts of the condensation products, act as antioxidants, tending to prevent the formation of corrosive acidity.

Although the phenolic condensation products appear to impart some detergency characteristics to oils, the metal salts of such condensation products do have an improved detergent action and in this respect appear to act as "soaps."

By the term "oil-soluble" is meant either the ability to enter into substantially true solution, or to be so completely dispersed as to avoid substantial clouding or separation when mixed with lubricating oil.

Where it is desired to obtain exceptional detergency sufficient to prevent the deposition of resinous and varnish-like materials upon the pistons, rings, valves and the like in severe service engines, it is desirable to employ along with the substituted phenol-acetylene condensation products or salts thereof small amounts of detergent materials which cooperate with the additives of this invention to impart the desired improved detergency characteristics to the resulting oil. Therefore, the invention also encompasses the use of the indicated hydrocarbon substituted phenol-acetylene condensation products and/or metal salts thereof in the indicated proportions in combination with between about 0.2% and as high as about 10 or 15% by weight of a detergent material, as for example an oil-soluble metal sulfonate or metal salt of a carboxylic acid, as for example a soap-forming fatty acid or modified fatty acid, naphthenic acid, rosin acid, synthetic petroleum acid formed by the oxidation of petroleum fractions such as solvent-treated paraffinic-type lubricating oil fractions, paraffin wax and the like. Included in the group of detergents which may be employed in conjunction with the

condensation products, and particularly the metal salts of the condensation products of this invention, are the oil-soluble complexes obtained by heating and dehydrating mixtures of oil-soluble sulfonic acids or metal salts of sulfonic acids with basically reacting metal compounds, as for example metal oxides, hydroxides, carbonates and bicarbonates.

Examples of detergent additives which cooperate with the additives of this invention to produce outstanding lubricating oils are calcium sulfonate, barium sulfonate, lead sulfonate, oil-soluble complexes consisting of calcium sulfonate-sodium carbonate, lead sulfonate-lead oxide, barium sulfonate-barium hydroxide and like materials.

Metals of the metal salts of the oil-soluble substituted phenol-acetylene condensation products and of the oil-soluble metal salts or soaps employed as supplemental detergents are preferably polyvalent metals and the metals of group II of the periodic table, including the alkaline earth metals calcium, strontium, barium and magnesium as well as zinc and cadmium, form the preferred group. Of this group of metals the alkaline earth metals are generally the most practical and thus form a restricted preferred group. Other polyvalent metals may be employed however, and thus are to be considered within the scope of this invention. Such metals include copper, zinc, aluminum, cobalt, nickel, iron, manganese, chromium, tin and the like. In fact, all of the polyvalent metals capable of forming oil-soluble metal salts of the condensation products of this invention may be used to obtain at least some of the advantages of the invention. Moreover, the alkali metals, e. g. sodium, potassium and lithium, may be employed in some instances since the alkali metal salts of the condensation products of this invention have been shown to possess at least some of the characteristics defined as being desirable when added to mineral lubricating oils. However, these metals are not to be considered the full equivalent of the polyvalent metals in this regard.

Although for most purposes the condensation products or particularly the metal salts of the condensation products of this invention impart adequate anti-corrosion characteristics to lubricating oils, for certain applications it is sometimes desirable to include supplemental anti-corrosion agents in the finished lubricating oils which cooperate with the condensation product salts. In such cases the metal salts of alkyl substituted phenol sulfides or alkylated phenol thioethers are the preferred agents. These materials fall under the class of compounds generally referred to as oil-soluble metal salts or soaps of high molecular weight weak non-carboxylic organic acids having an ionization constant below about 5×10^{-6}. Other agents of this general group such as the metal salts of thio-phenols, alcohols, enols, oximes and the like may be used. Also oil-soluble metal salts of substituted thiophosphates may be employed and are found to improve anticorrosion characteristics without deleteriously affecting the detergency and other desirable characteristics of the condensation product salts. These thiophosphate salts are prepared by treating organic compounds, particularly those having a hydroxyl group, with P_2S_5 or other phosphorus sulfide and neutralizing the resultant acid product.

Still another class of anticorrosion agents, which are particularly desirable because they do not impart an ash content to the oil, includes sulfurized terpenes, e. g., alphapinene, dipentene, and the like as well as natural mixtures of terpenes such as are found in turpentine and the like. Such materials are prepared by heating the terpene with 20% to 100%, based on the terpene, of sulfur to yield a product containing from 15% to 50% by weight of combined sulfur.

In addition to the employment of the above salts and soaps the invention also includes the use of other oiliness or film strength agents therewith. For example, either type of salt or soap may contain also chlorine or other halogen or sulfur or phosphorus as a substituent in the phenyl group of the phenol-acetylene condensation product or in the organic group of the detergent soap as the case may be. Moreover, if required a neutral common solvent may be employed to increase the solubility of the metal salt or soap in the oil. The latter requirement may be important where employing certain types of detergent soaps in highly paraffinic oils where solubility of the soaps in such oils is not adequate. Examples of such common solvents are diethylene glycol mono oleate, octyl acetate, diethylene glycol mono laurate, and diethylene glycol mono butyl ether.

The mineral lubricating oil to be employed may be either a naphthenic type oil or a paraffinic type oil insofar as the salt of the phenolic condensation product or resin is concerned, because these materials are highly soluble in both types of oil. Where a naphthenic oil is employed it may be a California or other oil of this type which may characteristically contain about 0.5% of organically combined sulfur naturally occurring therein or may contain as little as about 0.15% up to 4% or 5%, for example, 2.75% sulfur as in Santa Maria Valley (California) lubricating oils. The paraffinic type oil may be either a typical paraffin base oil such as a Pennsylvania oil, or a heavily solvent refined oil possessing highly paraffinic characteristics.

When adding the phenolic condensation product of this invention it is desirable to employ enough to give the effect, for example, 0.75%, but the upper limit, for example approaching 15%, should be restricted so that it does not cause undesirable thickening of the oil either alone or in conjunction with the "detergent" soap if added. Otherwise, it may become necessary to employ a neutral common solvent as above indicated.

In practicing the invention a suitable condensation product of a hydrocarbon substituted phenol (e. g. amyl phenol with acetylene) may be manufactured and appropriate oil-soluble salts such as the calcium salts produced therefrom. For example, the condensation product of p-tertiary amyl phenol with acetylene is prepared by contacting this phenol with acetylene at a temperature of about 200° C. under a pressure of about 15 to 20 atmospheres until the reaction mixture absorbs about 1 mol of acetylene per mol of the phenol. In this case a liquid resinous material is obtained which is oil-soluble and which is readily converted to its metal salt by treatment with hydrated lime, the metal salt also being oil-soluble.

Extreme care must be exercized in carrying out the condensation reactions because of the tendency for acetylene to explode when present in concentrations above about 40% or 50% when handled under pressure. Precautions to be observed in handling acetylene under pressure are

discussed by W. E. Hanford et al., Ind. Eng. Chem., vol 40, pages 1171 to 1177 (1948). In carrying out the condensation, therefore, the phenol is first placed in an autoclave or other pressure vessel and the vessel flushed with nitrogen or carbon dioxide or other inert diluent gas to substantially completely remove oxygen and the pressure vessel then pressured with nitrogen or the like to about 5 to about 15 atmospheres, depending on the temperature. Acetylene is introduced into the vessel pressured in this manner, care being taken to maintain an acetylene content not greater than about 25% or 30%, additional acetylene being introduced as the condensation reaction proceeds. Thus, after once having pressured the vessel with an inert gas, acetylene may be introduced at such a rate, either continuously or intermittently, as will maintain a pressure somewhat above that pressure obtained with the inert gas, until the desired quantity of acetylene has been absorbed.

The condensation may be carried out at ordinary temperatures but it is preferably effected at temperatures between about 100° C. and about 300° C. The preferred method of operation is to introduce the hydrocarbon substituted phenol into the autoclave, which should be of the rocking type to permit agitation, the autoclave is then flushed with nitrogen and pressured to about 3 to about 10 atmospheres with nitrogen and then to about 5 to about 15 atmospheres pressure with acetylene, taking care not to obtain an acetylene content of over about 30%. The autoclave is then heated to a temperature of 100° C. to 300° C., depending upon the original pressure, to obtain a maximum pressure of not more than about 25 to 30 atmospheres. As the pressure decreases due to absorption of acetylene the autoclave is again repressured and this repressuring is repeated until the desired amount of acetylene has been absorbed. The amount of acetylene absorbed during the reaction should be between about 0.5 mol and 1.5 or 2 mols per mol of phenol. Particularly desirable condensation products are obtained when the ratio is between 0.8 and 1.4 mols per mol of phenol.

Although the condensation reaction will proceed slowly in the absence of catalytic agents, in order to obtain practical reaction rates it is necessary to employ condensation catalysts. Active catalysts include particularly zinc and cadmium salts of carboxylic acids. Zinc and cadmium naphthenates having a metal content of around 10% to 15%, as for example about 12%, are found to be particularly satisfactory catalysts. Other metal salts of carboxylic acids may be employed, such other metals including iron, cobalt, nickel, copper, chromium and other polyvalent metals. These salts will include the polyvalent metal acetates, propionates, butyrates, oleates, abietates, linoleates and the like, where the metal is preferably zinc or cadmium but may be any polyvalent metal.

Other catalysts which may be employed include the organic nitrogen compounds, particularly the amines. Primary, secondary and tertiary alkyl amines such as mono, di and trimethyl amines, methyl ethyl amine, methyl propyl amine, mono, di and triethyl, propyl, butyl, amyl and octyl amines and the like are the preferred class of organic nitrogen compounds. Other nitrogen compounds which may be used include the alkylol amines such as the ethanol amines, propanol amines and the like; the mixed alkyl-alkylol amines, e. g. methyl diethanol amine; cycloalkyl amines such as cyclohexyl amine; aromatic amines, i. e. aniline, N-methyl aniline and naphthyl amine; di and poly amines such as penta methylene diamine; nitrogen bases, e. g. pyridine, piperidine, quinoline and mixtures of nitrogen bases such as are obtained by extracting naphthenic mineral oil fractions with acids.

The amount of catalyst to be employed is preferably about 5% to 10%, although as little as 1% is capable of catalyzing the reaction and as much as 15% or more may be employed without deleteriously affecting the quality or character of the resulting condensation product.

The condensation reaction may be carried out in the presence of solvents. In such cases the hydrocarbon substituted phenol is conveniently dissolved in the solvent and the solution placed in the autoclave. Solvents to be employed must not react with the phenol or with acetylene under the conditions of condensation. The use of solvents facilitates handling the condensation product, particularly its removal from the autoclave and in some instances appears to increase reaction rates. Solvents which may be employed are preferably hydrocarbons such as pentane, hexane, cyclopentane, cyclohexane or mixtures of such hydrocarbons, as for example light petroleum naphthas or thinners, benzene, toluene, xylene and the like and higher boiling petroleum fractions such as lubricating oil fractions. Other solvents which may be used include alcohols, such as methanol, ethanol, butanol; ketones such as acetone and methyl ethyl ketone and esters such as ethyl acetate, isopropyl acetate and butyl acetate. The amount of solvent to be employed will generally be between about 0.2 part and 2 parts per part of phenol although smaller or even larger proportions may be employed.

By varying the conditions of condensation, i. e. temperature, pressure, catalyst, etc., and using substituted phenols of varying molecular weights it is possible to vary the characteristics of the resulting condensation products over a relatively wide range. Thus, the products may be liquid to solid, brittle resins. Preferably the conditions will be selected such that the condensation products are semi-solid to solid resins.

Following condensation the product may be dissolved in mineral lubricating oil to produce a finished lubricating oil or dissolved in about 0.5 to 5 or as much as 10 parts of oil to produce a concentrate which may be further diluted to produce a finished lubricating oil. In order to produce the preferred additive and lubricating oils, however, the condensation product is converted into its metal salt either before or after dilution with mineral lubricating oil and the metal salt dissolved in oil or the oil solution of metal salt diluted with further amounts of lubricating oil to produce the finished lubricant. Moreover, where the condensation reaction is effected in the presence of solvent the resulting solvent solution of condensation product may be neutralized with basic metal compound and the solvent separated as by distillation.

Neutralization of the hydrocarbon substituted phenol-acetylene condensation product to form the metal salts is effected by treating the condensation product with a basically reacting metal compound, i. e., an oxide, hydroxide, hydrated oxide, carbonate or bicarbonate of the desired metal. This reaction is effected in the presence of water and in order to prevent hydrolysis, particularly when employing weakly basic metal compounds, an alcohol such as ethyl or isopropyl alcohol may be added The mixture is heated to

a temperature between about 80° C. and 95° C. for a period of about 2 hours with agitation and the resulting product heated to remove water and filtered to remove excess base. If a solvent is present the solvent may be vaporized before or after filtration. The resulting condensation product salt, if prepared in the absence of mineral lubricating oil, is a brittle, solid resin. This resin may be dissolved directly in lubricating oils to produce concentrates. i. e. where the concentration of resin salt is between about 10–15% and about 50 or 60%, or it may be dissolved in larger quantities of oil to produce finished lubricants. If the condensation reaction is carried out in the presence of lubricating oil an oil solution of condensation product is obtained. This oil solution may be neutralized directly by adding an aqueous solution or aqueous slurry of basically reacting metal compound under the conditions referred to above. In this case it is usually desirable to add alcohol to aid in the neutralization.

Although the removal of catalysts from the condensation product is not generally necessary, since the small amounts of metal salt or organic base employed do not adversely affect the lubricating oils containing condensation products or salts thereof from which catalysts have not been removed, it is sometimes desirable to remove the catalysts, particularly the metal salts employed as catalysts, before preparing metal salts of the condensation products. Moreover, it is sometimes desirable, although not necessary, to remove unreacted substituted phenol from the condensation products. These two impurities may be removed by the following process. The condensation product, after removal from the autoclave, is diluted with a solvent or, if the condensation reaction is carried out in the presence of solvent, the resulting solvent solution of condensation product is heated and filtered with 2 to 10% by weight, based on the total solvent solution, of a bleaching clay at a temperature approximating the boiling point of the solvent employed and then filtered. The bleaching clay appears to remove the metal salts employed as catalysts Following filtration the solvent is distilled off and if desirable the distillation is continued at reduced pressures, as for example pressures of 1 to about 25 mm. of mercury to temperatures sufficient to vaporize unreacted phenolic compound. Generally the removal of unreacted phenolic compound is not essential where the product is to be employed as a lubricating oil addition agent so that, following filtration, it is sufficient to distill off the solvent, leaving the catalyst-free condensation product.

In some cases the production of the desired metal salt is difficult by ordinary neutralization processes but may be readily effected by first forming the alkali metal salt of the condensation product and converting the alkali metal salt to the desired polyvalent metal salt by methathesis. Thus, the resin may be neutralized with aqueous soduim hydroxide, preferably in the presence of alcohol, and the resulting sodium salts converted to polyvalent metal salts by treatment with an inorganic salt of the desired metal. For example, in preparing zinc salts it is usually desirable to first prepare the sodium salt and add to the sodium salt an alcoholic solution of zinc chloride or nitrate. The methathesis is effected at ordinary temperature or at elevated temperatures in the range of about 50° C. to 100° C. in the presence of alcohol, and preferably a hydrocarbon solvent or lubricating oil. Methathesis results in the conversion of the sodium salt to the zinc salt, with precipitation of solid sodium salts which may be removed by filtration. Thus, the hydrocarbon or lubricating oil solution is heated to vaporize alcohol and filtered, preferably through a filtering clay. If a hydrocarbon solvent other than mineral lubricating oil is present this may be removed by distillation.

It is also possible to prepare the desired oil-soluble metal salts of hydrocarbon substituted phenol-acetylene condensation products by first converting the phenols into their metal salts and subsequently carrying out the condensation reaction. The conditions under which this reaction may be effected are similar to those described above for the phenol per se. However, the amount of catalysts to be employed may be reduced when operating in this manner and, in fact, condensation may be effected at reasonable rates without using catalysts when the metal phenates are employed.

In preparing the finished lubricants the condensation products or preferably the metal salts thereof or lubricating oil concentrates of such resins or metal salts are added to mineral lubricating oils in the desired quantity and dispersed or dissolved therein by agitation of the mixture. Preferably the oil will be heated to a temperature of 95° C. to 150° C. to increase the rate of solution. However, no special precautions are necessary because these materials are substantially oil-soluble or oil-dispersible and do not require unusual treatments to effect the desired solution. In some instances it is desirable to employ the metal salts of the condensation products together with unneutralized condensation products. In such cases the total additive content of a finished lubricating oil due to condensation product and salts thereof will be the same as that described hereinabove for either one of these additive materials alone. Amounts of supplemental anticorrosion agents which may be used will be between 0.2% and about 10% by weight. When these agents are metal salts the metals may be any of those disclosed for preparing the metal salts of this invention.

Lubricating oils containing the oil-soluble metal salts of hydrocarbon substituted phenol-acetylene condensation products and containing the condensation products themselves 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 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 will serve to illustrate further my invention but are not to be taken as in any way limiting the broader aspects of the invention.

Example I

A stainless steel autoclave having means for agitation is charged with 2060 g. (10 mols) of p-1,1,3,3-tetramethyl butyl phenol (an octyl phenol) and 19 g. (0.01 mols) of anhydrous zinc acetate. The autoclave is sealed and air is completely removed by flushing with nitrogen. The contents of the autoclave are then heated to 200° C. and the pressure in the autoclave is adjusted to about 9.5 atmospheres pressure with nitrogen. Maintaining a temperature of about 200° C. acetylene is introduced into the autoclave until the pressure is approximately 14 atmospheres and a pressure of between about 10 and 15 atmospheres is maintained by continuously introducing acetylene into the autoclave as it is absorbed. When approximately 260 g. (10 mols) of acetylene have been absorbed the autoclave is flushed with nitrogen, the pressure released and the contents removed. The product, amounting to approximately 2300 g., is a brown solid resin at ordinary temperatures having a softening point of about 115° C.

A 100 g. portion of the resin is dissolved in 1900 g. of a highly solvent treated Western paraffinic lubricating oil of SAE 30 grade to produce an oil containing 5% by weight of the octyl phenol-acetylene condensation product. This oil will be referred to as Oil A.

A second 100 g. portion of the resin and 100 g. of an oil concentrate of calcium mahogany sulfonate containing about 40% by weight of the sulfonate are dissolved in 1800 g. of the same lubricating oil to produce an oil containing 5% by weight of the condensation product and 2% by weight of sulfonate. This oil will be referred to as Oil B. Lauson engine tests made on these oils and for comparison on the base oil without additives give the following results:

Lubricating Oil	Detergency at 60 Hrs., Per Cent	Bearing Weight Loss, Mgs., at—		
		20 Hrs.	40 Hrs.	60 Hrs.
Base Oil	58	200	400	(1)
Oil A	65	30	150	345
Oil B	85	25	165	390

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

Example II

A 200 g. portion of the condensation product from Example I is dissolved in 800 g. of a highly solvent-refined Western paraffinic mineral lubricating oil of SAE 30 grade by stirring at 150° C. This solution is heated with stirring at about 100° C. for 2 hours with 31 g. of calcium hydroxide and 30 ml. of water. The temperature is then increased to about 175° C. to remove water and the product is filtered through diatomaceous earth to remove unreacted calcium hydroxide. The filtrate is a clear oil solution containing approximately 20% by weight of the calcium salt of the octyl phenolacetylene condensation product.

A lubricataing oil prepared by dissolving 400 g. of the above calcium salt concentrate in 2000 g. of the same lubricating oil used above has a detergency of 67% and a bearing weight loss at 60 hours of 180 mg. as indicated by a Lauson engine test.

A lubricating oil prepared by dissolving 400 g. of the above calcium salt concentrate, 50 g. of calcium mahogany sulfonate and 50 grams of calcium tert. butyl diphenol sulfide in 1900 g. of the lubricating oil referred to in Example I as base oil has a detergency of 87% and a bearing weight loss at 60 hours in the Lauson engine test of 150.

Example III

A 200 g. portion of the condensation product prepared in Example I is dissolved in 1 liter of a paraffinic hydrocarbon solvent consisting primarily of heptanes by heating at refluxing temperatures. The lead salt of the condensation product is produced by adding 94 g. of lead monoxide and 25 ml. of water to the solvent solution of condensation product and refluxing the mixture for 3 hours. At this time a water trap is placed in the reflux stream and refluxing is continued until no further water is collected in the trap. The mixture is cooled to room temperature, filtered through diatomaceous earth to remove unreacted lead oxide and then evaporated to remove the hydrocarbon solvent. The product is a brittle solid consisting of the lead salt of octyl phenolacetylene condensation product. A lubricating oil prepared by dissolving 130 g. of the above product in 2000 g. of the highly solvent treated paraffinic Western mineral lubricating oil of SAE 30 grade referred to in Example I as base oil has a detergency of 62% and a bearing weight loss of 155 mg. at 60 hours in the Lauson engine test.

A lubricating oil prepared by dissolving 130 g. of the above lead salt and 100 g. of an oil concentrate of calcium mahogany sulfonate containing about 40% by weight of the sulfonate in 1900 g. of the same base oil has a detergency of 89% and a bearing weight loss at 60 hours of 160 mg.

A lubricating oil prepared by dissolving 130 g. of the above lead salt and 100 g. of a lead sulfonate-lead oxide complex, prepared by heating 1 equivalent of lead sulfonate with 1 equivalent of lead oxide in the presence of water and mineral oil to a temperature of about 150° C. until the product was dehydrated and filtering the resulting product, in 2000 g. of the mineral lubricating oil referred to as base oil has a detergency of 95% and a bearing weight loss of 150 mg. at 60 hours in the Lauson engine test.

Example IV

A 400 g. portion of the condensation product obtained in Example I is dissolved in 1600 g. of an SAE 30 mineral oil of the type described in Example II. To this oil solution is added 135 g. of a 50% aqueous sodium hydroxide solution and the mixture heated with stirring at about 105°–110° C. to effect neutralization and subsequently heated to about 200° C. and filtered through diatomaceous earth to yield as filtrate

an oil solution containing approximately 20% by weight of the sodium salt of octyl phenol-acetylene condensation product.

A lubricating oil prepared by dissolving 400 g. of the above sodium salt concentrate in 1600 g. of the base oil employed in the above examples has a detergency of 57% and a bearing weight loss of 400 mg. at 60 hours in the Lauson engine test.

Example V

Approximately one-half of the oil solution of sodium salt prepared in Example IV is stirred vigorously with a solution containing 58 g. of anhydrous zinc chloride dissolved in isopropanol. A white precipitate immediately appears. After stirring for about 2 hours at room temperature the mixture is heated to 150° C. and filtered through diatomaceous earth to yield as filtrate a solution containing approximately 20% by weight of the zinc salt of octyl phenol-acetylene condensation product.

A lubricating oil prepared by dissolving 400 g. of the above zinc salt concentrate in 2,000 g. of base oil has a detergency of 65% and a bearing weight loss of 182 mg. in the Lauson engine test.

Example VI

A butyl phenol-acetylene condensation product is prepared by reacting a mixture of 750 g. (5 mols) of p-tert. butyl phenol and 58 g. of zinc naphthenate containing about 11% by weight of zinc with acetylene under the conditions described in Example I. The product is a tan brittle resin having a softening point of about 125° C. This product is dissolved in 4000 ml. of benzene and stirred at about 50° C. with 200 g. of a surface active clay. The mixture is then cooled to room temperature and filtered to remove the clay together with materials adsorbed by the clay. The filtrate is evaporated to remove the benzene and then distilled in vacuum to a bottoms temperature of 200° C. at a pressure of 2 mm. of mercury to remove unreacted butyl phenol. The residue is a clear brittle resin having a softening point of about 120° C.

This purified product is dissolved in 7000 g. of the SAE 30 mineral lubricating oil referred to above as base oil by heating and stirring at a temperature of about 150° C. The oil solution is heated at about 105° C. with 425 g. of anhydrous barium hydroxide and 150 ml. of water for 3 hours and then heated to about 175° C. and filtered through diatomaceous earth to yield as filtrate an oil solution containing about 15% by weight of the barium salt of butyl phenol-acetylene condensation product.

A lubricating oil prepared by dissolving 400 g. of the above barium salt concentrate in 1600 g. of the above mentioned base oil has a detergency of 64% and a bearing weight loss of 190 mg. in the Lauson engine test.

A lubricating oil prepared by dissolving 400 g. of the above barium salt concentrate and 50 g. of barium mahogany sulfonate in 1550 g. of base oil has a detergency of 88% and a bearing weight loss of 200 mg. at 60 hours.

A lubricating oil prepared by dissolving 400 g. of the above barium salt concentrate and 50 g. of a commercial sulfurized terpene containing approximately 30% by weight of sulfur in 1550 g. of base oil has a detergency of 55% and a bearing weight loss of 85 mg.

A lubricating oil prepared by dissolving 400 g. of the above barium salt concentrate, 50 g. of barium sulfonate and 50 g. of a commercial sulfurized terpene referred to above has a detergency of 84% and a bearing weight loss of 90 mg. at 60 hours in the Lauson engine test.

Example VII

A phenol-acetylene condensation product prepared by reacting beta-phenyl ethyl phenol with acetylene at a pressure of 20 atmospheres and at a temperature of 200° C. using a cadmium naphthenate catalyst following the procedure described in Example I gives a resin of similar properties to that produced in Example I.

The calcium salt of the above resin dissolved in lubricating oil to produce an oil containing 2% by weight of the salt produces an oil having improved anticorrosion characteristics.

Example VIII

Example I repeated using 1 part of benzene per part of octyl phenol as solvent during the condensation gives a benzene solution of a resin which, when the benzene is evaporated, leaves a resin having a softening point of about 110° C. and otherwise similar to the resin of Example I.

Example IX

A stainless steel autoclave is charged with 1500 g. (10 mols) of p-tert. butyl phenol, 1500 g. of an SAE 30 paraffinic mineral lubricating oil and 100 g. of cadmium naphthenate. Air is completely removed from the autoclave by flushing with nitrogen and the autoclave is then pressured with nitrogen to about 8 atmospheres. Acetylene is introduced into the autoclave until a pressure of about 12 atmospheres is obtained and the contents heated to about 170° F. Additional acetylene is added until about 260 g. of acetylene have been absorbed. The autoclave is then cooled, flushed with nitrogen and the contents removed. The product consists of a concentrate of the butyl phenol-acetylene condensation product in oil containing approximately 55% by weight of the condensation product.

The above product is neutralized by treatment with hydrated lime at a temperature of about 110° C. and subsequently heated to 200° C. and filtered through diatomaceous earth.

100 g. portion of the above product is dissolved in 1000 g. of the SAE 30 base oil described in the preceding experiments and the resulting oil has a detergency of 65% and a bearing weight loss of 140 mg. at 60 hours in the Lauson engine test.

A second 100 g. portion of the calcium salt concentrate produced as above and 25 g. of the calcium salt of the acidic material obtained by reacting octyl alcohol with phosphorus pentasulfide are added to 1000 g. of the same base oil. This oil has a detergency of 60% and a bearing weight loss of 95 mg. at 60 hours in the Lauson engine test.

Example X

An equivalent amount of cyclohexyl phenol is substituted for the butyl phenol in Example IX and the resulting product, when converted to its calcium salt and added to lubricating oil in an amount sufficient to give an oil containing about 5% by weight of the calcium salt, produces an oil having improved 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 mineral lubricating oil containing a small proportion, between about 0.2% and about 15% by weight, of a compound selected from the class of compounds consisting of the oil-soluble condensation products of a hydrocarbon substituted phenol with acetylene and oil-soluble metal salts of said condensation products, said condensation product being obtained by reacting said phenol with acetylene at a temperature between atmospheric temperature and about 300° C. and at a pressure between about 5 and about 30 atmospheres for a time sufficient to absorb between about 0.5 and 2 mols of acetylene per mol of phenol.

2. A mineral lubricating oil containing a small proportion, in the order of about 0.2% to about 15% by weight, of the condensation product of a hydrocarbon substituted phenol with acetylene, said condensation product being obtained by reacting said phenol with acetylene at a temperature between about 100° C. and about 300° C. and at a pressure between about 5 and about 25 atmospheres until between about 0.8 and about 1.4 mols of acetylene per mol of phenol have been absorbed by the reaction mixture.

3. A mineral lubricating oil containing between about 0.2% and about 15% by weight of an oil-soluble metal salt of the condensation product of a hydrocarbon substituted phenol with acetylene, said condensation product being obtained by reacting said phenol with acetylene at a temperature between about 100° C. and about 300° C. and at a pressure between about 5 and about 25 atmospheres until between about 0.8 and about 1.4 mols of acetylene per mol of phenol have been absorbed by the reaction mixture.

4. A mineral lubricating oil containing between about 0.2% and about 15% by weight of an oil-soluble metal salt of the condensation product of an alkyl phenol with acetylene, said condensation product being obtained by reacting the alkyl phenol with acetylene at a temperature between about 100° C. and about 300° C. under a pressure between about 15 and about 20 atmospheres until the reaction mixture has absorbed about 1 mol of acetylene per mol of phenol.

5. A mineral lubricating oil containing between about 0.2% and about 15% by weight of a polyvalent metal salt of the condensation product of an alkyl phenol with acetylene, wherein the alkyl substituent contains at least 3 carbon atoms to insure solubility of the salt in the lubricating oil, said condensation product being obtained by reacting said phenol with acetylene at a temperature between atmospheric temperature and about 300° C. and at a pressure between about 5 and about 30 atmospheres for a time sufficient to absorb between about 0.5 and 2 mols of acetylene per mol of phenol.

6. A mineral lubricating oil according to claim 5 in which the polyvalent metal is a metal of group II of the periodic table.

7. A mineral lubricating oil according to claim 5 in which the polyvalent metal is an alkaline earth metal.

8. A mineral lubricating oil according to claim 5 in which the polyvalent metal is calcium.

9. A mineral lubricating oil according to claim 5 in which the polyvalent metal is barium.

10. A mineral lubricating oil according to claim 5 in which the polyvalent metal is lead.

11. A mineral lubricating oil according to claim 5 containing also between about 0.2% and 10% by weight of an oil-soluble metal petroleum sulfonate.

12. A mineral lubricating oil according to claim 5 containing also between about 0.2% and about 10% by weight of a sulfurized terpene.

13. A mineral lubricating oil containing between about 0.2% and about 15% by weight of a polyvalent metal salt of the condensation product of an alkyl phenol with acetylene, wherein the mol ratio of acetylene to alkyl phenol is between about 0.5 and 2 to 1, said condensation product being obtained by reacting said phenol with acetylene at temperatures between atmospheric temperature and about 300° C. and at pressures between about 5 and about 30 atmospheres.

14. A mineral lubricating oil containing between about 0.5% and about 10% by weight of an oil-soluble polyvalent metal salt of the condensation product of an alkyl phenol with acetylene, wherein the mol ratio of acetylene to phenol is between about 0.8 and 1.4 to 1, said condensation product being obtained by reacting said phenol with acetylene at temperatures between atmospheric temperature and about 300° C. and at pressures between about 5 and about 30 atmospheres.

15. A mineral lubricating oil according to claim 14 containing also between about 0.2% and 10% by weight of an oil-soluble metal petroleum sulfonate.

16. A mineral lubricating oil according to claim 14 containing also between about 0.2% and 10% by weight each of an oil-soluble metal petroleum sulfonate and a sulfurized terpene.

17. A mineral lubricating oil containing between about 0.5% and about 10% by weight of a polyvalent metal salt of the condensation product of a hydrocarbon substituted phenol with acetylene, wherein the hydrocarbon substituents of the phenol contain at least 4 carbon atoms said condensation product containing a ratio of between 0.5 and 2 mols of acetylene per mol of phenol and being obtained by reacting said phenol with acetylene at a temperature between atmospheric temperature and about 300° C. and at a pressure between about 5 and about 30 atmospheres.

18. A mineral lubricating oil according to claim 17 in which the hydrocarbon substituted phenol contains a cycloalkyl substituent.

19. A mineral lubricating oil according to claim 17 in which the phenol contains an aralkyl group.

20. A mineral lubricating oil containing 0.5% to 10% by weight of an oil-soluble polyvalent metal salt of the condensation product of an alkyl phenol with acetylene and between 0.2% and 10% of a detergent selected from the class of detergents consisting of oil-soluble metal petroleum sulfonate and oil-soluble complexes of metal sulfonate with basically reacting inorganic metal compound said condensation product containing a ratio of between 0.5 and 2 mols of acetylene per mol of phenol and being obtained by reacting said phenol with acetylene at a temperature between atmospheric temperature and about 300° C. and at a pressure between about 5 and about 30 atmospheres.

21. A mineral lubricating oil containing between about 0.2% and about 15% by weight of the barium salt of the condensation product obtained by condensing p-tertiary butylphenol with

acetylene at a temperature of about 200° C. under a pressure of about 15 to about 20 atmospheres until the reaction mixture has absorbed about 1 mol of acetylene per mol of phenol.

22. A method for preparing mineral lubricating oil having anti-corrosion characteristics which consists in condensing a hydrocarbon substituted phenol with acetylene at temperatures between atmospheric temperature and about 300° C. and at pressures between about 5 and about 30 atmospheres to form an oil-soluble condensation product containing a ratio of acetylene to phenol of between 0.8 and 1.4 to 1 and dissolving between about 0.2% and about 15% by weight of said oil-soluble condensation product in mineral lubricating oil.

23. A method for preparing mineral lubricating oil having anti-corrosion characteristics which consists in condensing an alkyl substituted phenol with acetylene at temperatures between atmospheric temperature and about 300° C. and at pressures between about 5 and about 30 atmospheres to produce an oil-soluble condensation product containing a ratio of acetylene to phenol of between 0.8 and 1.4 to 1 and dissolving between about 0.2% and about 15% by weight of said condensation product and between about 0.2% and about 10% by weight of an oil-soluble metal petroleum sulfonate in mineral lubricating oil.

24. A method for preparing mineral lubricating oil having anti-corrosion characteristics which consists in condensing an alkyl substituted phenol with acetylene wherein the mol ratio of acetylene to alkyl phenol is between about 0.5 and 2:1 to produce an oil-soluble condensation product and dissolving between about 0.2% and about 15% by weight of said oil-soluble condensation product in mineral lubricating oil, the condensation being affected at temperatures between about 100° C. and about 300° C. and at a pressure less than about 30 atmospheres.

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