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PROCESS OF PREPARING LUBRICATING OIL ADDITIVES BY OXIDATION OF HIGH MOLECULAR WEIGHT HYDROCARBONS WITH NITRIC ACID

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This invention relates to lubricating compositions. In one of its more specific aspects, this invention relates to petroleum lubricating oil compositions. In another of its more specific aspects, this invention relates to an "ashless" lubricant additive having detergent and/or dispersant properties and being suitable for use in lubricating compositions. In another of its more specific aspects, this invention relates to a method for the production of an "ashless" lubricant additive suitable for use in petroleum lubricant compositions. In still another of its more specific aspects, this invention relates to an "ashless" detergent suitable for use in lubricating oil compositions and prepared from selected hydrocarbon materials containing a component having a viscosity of at least 45 SUS at 210° F.

As the speed and output of internal combustion engines have been gradually increased to higher and higher values, the ability of non-additive oils to adequately take care of the lubrication and to maintain an engine free from lacquer, sludge and carbon deposits has continued to decrease. Metal-containing detergents such as barium or calcium sulfonates or phenates have been extensively used. These have served satisfactorily in many cases as the concentrations used were low or only moderately high. As cleanliness requirements called for still greater concentration of detergent additive, the problem of ash deposition in the combustion chamber became more serious. Especially is this a problem in certain engines which tend to develop preignition troubles in the presence of metallic ash. Also, in high-output aircraft engines, oils containing detergent additives have never been permitted for the same reason.

The requirements desirable in a satisfactory detergent additive are: (1) compatibility with lubricating oil and other types of additives which may be present; (2) maintenance of satisfactory cleanliness of the engine parts, principally in the ring belt zone of the piston; (3) chemical inertness with respect to supplemental additives and metal engine parts. Additional desirable characteristics include: (1) ease of handling, either as such or as an oil concentrate; (2) minimum effect on oil properties such as viscosity, color and odor; (3) inexpensive overall cost; (4) independence with respect to critically limited or expensive raw materials.

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

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problems normally encountered in internal combustion engines in connection with metal-containing deposits.

The use of additives in lubricating compositions as corrosion inhibitors, oxidation inhibitors, viscosity index improvers, dispersing agents, pour-point depressants, extreme pressure agents, lubricity improvers and ash forming detergents, is well known. The need for additives to improve various specific properties of lubricating oils is all the more acute and necessary in view of the service conditions which lubricating oils undergo and must withstand. In internal combustion engines such as automotive, aviation and diesel engines it is desirable that the lubricating compositions be resistant to sludge and varnish formation and in the event of such formation, to prevent the deposition of those materials on metallic parts of the engine.

This application is a continuation-in-part of my co-pending application Serial Number 304,659, filed August 15, 1952, now abandoned, wherein there is disclosed and claimed an additive for lubricating oils which is useful as a detergent or dispersant therein produced by the oxidation of a selected hydrocarbon fraction having at least 40 carbon atoms per molecule. One material well suited for the production of the ashless detergent by oxidation thereof is preferably one which is substantially saturated and contains at least 40 carbon atoms per molecule, preferably between 40 and 80 carbon atoms per molecule. The hydrocarbon material should have a refractive index of between 1.440 and 1.520. Hydrocarbon materials which may be satisfactorily used in the preparation of the ashless detergent include substantially saturated diene polymers, such as polybutadiene, and olefin polymers having from 2 to 12 carbon atoms per monomer molecule, such as polypentadiene, polypropylene, polyethylene, polyisobutylene, etc., preferably having a ratio of carbon atoms to olefin bonds of at least 40 to 1 and not less than 16 to 1, copolymers such as styrene-olefin copolymers, alkylated polystyrene, and a petroleum lubricating oil fraction which has substantially no asphalt, either in its natural state or when deasphalted, and which has been solvent extracted to reduce the content of aromatic-type hydrocarbons therein, and preferably dewaxed.

The detergent-type lubricating oil additives may be used singly or in combination. These materials contain one or in combination two or more materials such as substantially neutral completely organic, oxygen-containing compounds such as alcohols, esters, ethers, lactones, anhydrides, ketones, and aldehydes. Examination of the oxidized materials by infrared spectroscopy discloses very marked changes in the absorption bands upon oxidation of the selected hydrocarbon fractions disclosed herein. A very strong carbonyl band within the 5.76 to 5.87 micron region is produced in the initial oxidation of the hydrocarbon as is a weak absorption band at 2.94 to about 3.0 which indicates the presence of a low concentration of hydroxyl groups. These bands are characteristic of a concentrated oxidized product but also appear in the scanning of the total oxidized hydrocarbon fraction. The concentrated oxidized material also exhibited a broad absorption band in the 7-10 micron region, this band being much weaker for the unconcentrated material.

Petroleum fractions which are suitable for oxidation to produce the ashless detergent for use in lubricating oils, include Pennsylvania, Mid-Continent, California, East Texas, Gulf Coast, Venezuela, Borneo, and Arabian crudes. The source of the crude from which the petroleum fraction is derived does not significantly influence the preparation or properties of the ashless detergent material provided the petroleum fraction has been prepared by subjecting the crude to certain neces-

sary treatments to exclude undesired materials therefrom.

In the preparation of the preferred petroleum fraction from which the detergent material is produced, a crude oil is topped, i.e., distilled to remove therefrom the more volatile, lower molecular weight hydrocarbons such as gasoline and light gas oil, and then vacuum reduced to remove heavy gas oil and light lubricating oil of the SAE 10 and 20 viscosity grade. The vacuum reduced crude is then propane fractionated to remove an overhead fraction of about 100 SUS at 210° F. viscosity and the residual material is subjected to a second propane fractionation to remove another overhead fraction of about 200 SUS at 210° F. viscosity. The residue from the second fractionation may be subjected to a third propane fractionation to remove still another overhead fraction of about 575 SUS at 210° F. viscosity. Propane fractionation may be modified by the presence of butane, ethane or methane to the extent desired.

Following the propane fractionation step the overhead oil fraction is solvent extracted with a selective solvent which will separate the paraffinic hydrocarbons from the more aromatic-type hydrocarbons. Suitable selective solvents for aromatic hydrocarbons include among others the various phenols, sulfur dioxide, furfural and β,β' -dichlorodiethyl ether. The solvent extraction step for the removal of the more highly aromatic compounds can be carried out in accordance with the well-known concurrent or countercurrent solvent extraction techniques as well as by the well-known Duo-Sol technique.

The resulting solvent extracted material, before or after the removal of the more aromatic hydrocarbons, is preferably dewaxed. Dewaxing may be carried out by any conventional method, e.g. by solvent dewaxing using propane or solvent mixture such as methyl ethyl ketone or methyl isobutyl ketone with benzene at a suitable temperature.

Each of the phenol extracted, dewaxed, propane-fractionated oils have been used in preparing the detergent material of this invention with good results but the oil fraction from the second propane fractionation is preferred. It will be recognized by those skilled in the art that propane fractionated oils differing from those described may be used or a single broad viscosity cut can be used. The residual material from the final propane fractionation contains the rejected asphalt and more aromatic oils.

Although the preferred method for preparation of feed stock is as above described, other methods may be used to secure a similar type hydrocarbon fraction. Thus, a vacuum reduced crude which has essentially no asphalt, such as a Pennsylvania oil, may be used directly or after a light acid treatment. Another method, while not feasible commercially at the present time, is ultra-high vacuum (molecular) distillation to obtain the desired fraction described more exactly in subsequent paragraphs.

As pointed out above, a polydiene such as liquid polybutadiene which is prepared by sodium-catalyzed polymerization of butadiene and which material is subsequently hydrogenated so as to reduce the olefinic unsaturation thereof to a desired amount, is another suitable feed stock for use in the production of the detergent material. When butadiene is polymerized, only one double bond remains therein for each butadiene group of the polymer. The feed material should be hydrogenated sufficiently so that the ratio of carbon atoms to double bonds is at least 16 to 1. Preparation of liquid polybutadiene may be obtained by means of the process set forth in U.S. application Serial No. 67,098, filed December 23, 1948, by W. W. Crouch.

Another suitable feed stock is a liquid or semi-solid polybutadiene which is prepared by conventional emulsion polymerization and coagulation to form synthetic rubber and which material is subsequently hydrogenated so as to reduce the olefinic unsaturation thereof to the

desired amount and finally thermally depolymerized sufficiently to increase the ease of oxidation and to increase the oil solubility.

Another suitable feed material is a high molecular weight polymer prepared by zirconium tetrachloride polymerization of propylene. Still another material which has proved to be useful as a feed material for the oxidation step in the preparation of the detergent material is a "tacky polymer" prepared by the polymerization of propylene over chromia-silica-alumina catalyst as more fully disclosed in U.S. application Serial No. 333,576, filed January 27, 1953, by John P. Hogan and Robert L. Banks. Another suitable feed material is a copolymer of styrene with olefins in which the olefin portion constitutes at least 50 percent of the total molecular weight of the molecule. With any of these feed materials, it is desired to reduce the amount of olefinic unsaturation to such an extent that the ratio of carbon atoms to olefinic bonds is preferably at least 40:1 and not less than 16:1. The hydrocarbon stocks which are useful for producing the detergent material include those materials which are identifiable as having the following properties set forth in Table 1.

TABLE 1

Property	Broad Range	Preferred Range
Refractive Index n_D^{20}	1.440-1.520	1.480-1.515
Average Molecular Weight.....	above 550	600-10,000
Minimum Molecular Weight.....	450	
Viscosity, SUS at 210° F.....	above 50	above 100
Viscosity Index (when determinable) ¹	50-125	80-120
Carbon Atom Content per Molecule.....	above 40	50-720

¹ Viscosity index not determinable for non-Newtonian materials.

The lubricating oil and polymers having a similar viscosity, which are suitable as feed stocks in my process are set forth in Table 2.

TABLE 2

Property	Broad Range	Preferred Range
Refractive Index n_D^{20}	1.440-1.520	1.480-1.515
Average Molecular Weight.....	550-1,300	600-900
Minimum Molecular Weight.....	450	
Viscosity, SUS at 210° F.....	50-1,400	100-600
Viscosity Index.....	50-125	80-120
Carbon Atom Content per Molecule.....	40-80	50-70

It appears that during oxidation, scission takes place in the large hydrocarbon molecules. This is substantiated by passing nitrogen gas through the oil at 250° C. and collecting the volatile products which were negligible. Only a very small amount was collected when the temperature was raised to 300° C., thus, demonstrating that the major cause of the formation of the volatile products is oxidation and not thermal decomposition nor stripping of light ends originally present in the oil. With oils of moderate molecular weight, scission can not take place in any position but what one or all of the fragments is sufficiently small that distillation takes place, thus preventing accumulation of molecules appreciably smaller than those originally present. Hence, the viscosity is not decreased to any great extent. Concomitant with the oxidative scission reaction there is a polymerization or condensation reaction resulting in an increase in viscosity. The net change in viscosity is apparently due to the relative magnitude of each reaction. In very high molecular weight hydrocarbons the oxidative scission more frequently results in fragments which have molecular weights too large to be removed by distillation and, hence, the molecular weight decreases causing a decrease in viscosity especially during the initial portions of the oxidation period. As the oxidation reaction proceeds, the reactions causing increased molecular weight may offset, more or less, those causing a decrease in molecular weight. As a result, the molecular weights of charge oils having molec-

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ular weights in the lower range tend to increase and those in the higher range tend to decrease during the initial oxidation period.

If desired, the petroleum oil fraction which has been highly refined as described above may be further subjected to additional refining treatments. For example, these petroleum fractions may be hydrogenated to convert any aromatic compounds therein to the corresponding naphthenic and saturated hydrocarbon, or if desired these petroleum fractions may be subjected to contact with silica gel for the preferential adsorption and removal of the more aromatic hydrocarbons therefrom. Generally, the petroleum fraction which is oxidized for the production of the ashless detergent should contain not more than 20 percent of the carbon atoms in aromatic rings as determined by ring analysis. It is preferred that the aromatic content of the petroleum fraction be reduced to an economically feasible extent by refining procedures since oxidation of aromatic-type hydrocarbons tend to result in the formation of oil-insoluble products not suitable for producing the detergent material. It also appears that aromatic constituents oxidize more readily than do the nonaromatic components. Thus, failure to remove the most aromatic materials from the feed before oxidation results in formation of considerable oil-insoluble materials. Usually a suitable petroleum fraction, upon distillation under reduced pressure, e.g., molecular distillation, will produce a first 10 percent by weight fraction which has a viscosity of more than 50 SUS at 210° F., preferably more than 80 SUS at 210° F.

Lubricating oils, such as highly refined petroleum bright stocks, which are employed in the oxidation reaction can be additionally treated so as to yield a desired, solid ashless detergent of improved color properties as more fully disclosed and claimed in my copending U.S. application Serial No. 264,840, filed January 3, 1952. The additive material which is produced without this type of treatment is very dark red in color. An outstanding improvement resulting from this additional treatment is that the ashless detergent product is much lighter in color than a product obtained without this treatment and does not produce as dark a color in a lubricating oil composition containing the same.

Broadly speaking, this additional treatment comprises treating the charge stock prior to oxidation by contacting it with silica gel or a similar solid selective adsorbent for the removal of the more aromatic hydrocarbon types. Accordingly a lubricating oil stock such as a petroleum bright stock which has substantially no asphalt, a low aromatic content and, preferably, low wax content is additionally treated with silica gel at about room temperature usually, in the range 40° F. to 170° F., and a sufficient pressure differential is maintained across the bed or mass of silica gel so as to cause a satisfactory flow therethrough of the lubricating oil fraction being treated. The charge stock which is thus treated may be any hydrocarbon fraction suitable for the production of the detergent additive, usually a hydrocarbon fraction having a viscosity in the range 70 to 700 SUS at 210° F., preferably a lubricating oil fraction in the range 115 to 300 SUS at 210° F. A highly refined lubricating oil in these ranges will generally have an average molecular weight in the range 550 to 1100. It is preferred that the hydrocarbon fraction contain no portion having a molecular weight below 450.

After contact of the oil with the silica gel an unadsorbed hydrocarbon fraction is obtained and a second fraction is obtained by desorbing the silica gel with pentane or other liquid saturated aliphatic hydrocarbon usually in the C₅ to C₈ range. The unadsorbed fraction and that fraction obtained by the initial desorption with the saturated aliphatic hydrocarbon is the preferred material which yields, upon oxidation, a solid ashless detergent product of improved color properties. By this additional silica gel treatment of the lubricating oil charge stock,

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it has been found that the percent of carbon atoms present in the aromatic rings of the oil treated in this manner is much smaller than that present in the original unpurified bright stock, and the preferred charge stock after this treatment has an increased viscosity index, being at least greater than 70 and usually at least 100. It is preferred that no fractional part of the fraction obtained by this treatment contain more than 15 percent and preferably no more than 5 percent of its carbon atoms in aromatic rings.

It has been found that materials which are useful as ashless detergents in lubricating oils are produced by oxidation of such an above-described selected hydrocarbon fraction. During the oxidation reaction for the production of the detergent material, the selected hydrocarbon fraction is modified, resulting in a product of increased dispersant activity which differs from the starting material in respect to the four following physical characteristics

- (1) An increase in the carbon to hydrogen weight ratio
- (2) An increase in molecular weight
- (3) An increase in the oxygen content
- (4) A decreased solubility in propane under propane fractionating conditions

All these changes are brought about by contacting an above-described selected hydrocarbon fraction under suitable conditions of temperature and pressure with an oxidizing agent such as free oxygen, sulfur trioxide, nitrogen dioxide, nitrogen trioxide, nitrogen pentoxide, acidified chromium oxides and chromates, permanganates, peroxides such as hydrogen peroxide, sodium peroxide and ozone. Any oxygen containing material capable of releasing free oxygen under the oxidizing conditions may be used. Suitable other specific oxidizing agents include air, relatively pure commercial grade oxygen, oxygen enriched air, and a mixture of oxygen with an inert gas, such as carbon dioxide and nitrogen. Even oxygen admixed with natural gas or methane is satisfactory. Air having less than the usual amount of oxygen may also be used. Air is economically a preferred oxidizing agent.

Generally the oxidation reaction is carried out at a temperature in the range of from -40° F. to 800° F. When using an active oxidizing agent such as sulfur trioxide, temperatures in the range of -40° F. to 400° F., preferably 70° F. to 200° F. are used. With less active oxidizing agents, such as air, higher temperatures are used, such as 100° F. to 800° F., preferably 390° F. to 575° F. Higher oxidation temperatures result in a faster oxidation reaction. When the oxidizing agent is in the gaseous phase, another variable which affects the rate of the oxidation reaction is the partial pressure of the oxidizing agent. Accordingly, as the pressure at which the oxidation reaction is carried out is increased, other conditions remaining the same, the oxidation reaction proceeds at a faster rate. Therefore depending upon the rate of oxidation desired, the oxidation reaction is carried out at sub-atmospheric, atmospheric or superatmospheric pressure. Usually it is preferred to carry out the oxidation reaction at a pressure between about 10 and 100 lbs. per square inch absolute depending upon the composition or oxygen content of the oxidizing gas. Lower or higher absolute pressures may be satisfactorily used if desired. Lower oxidation pressures are useful in that they facilitate release and removal of the more volatile, and other undesirable materials, e.g., H₂O from the reaction mixture.

The rate of oxidation is also dependent upon and influenced by the distribution of the oxidizing gas within the reaction mixture and the rate of introduction of the oxidizing gas thereto. The oxidizing agent is preferably introduced and present in the reaction mixture in a finely dispersed state in order to achieve better contact with the materials undergoing oxidation and better mixing therewith. An increase in the rate of introduction of the oxidizing gas of course increases the rate of oxidation, other conditions remaining unchanged. The conditions of tem-

perature, pressure, oxygen content of the oxidizing gas, rate of introduction of oxidizing gas, etc. are correlated, adjusted and controlled so as to carry out the oxidation reaction at a sufficiently rapid rate so as to minimize reaction time while readily and easily controlling the reaction.

Conditions which have been found to be satisfactory for producing the ashless detergent from a selected hydrocarbon fraction when using a moderate oxidizing agent, such as air, are set forth in Table 3.

TABLE 3

Reaction Condition	Broad Range	Preferred
Temperature, ° F.	100-800	375-575
Time of Oxidation, hrs.	3-75	5-50
Pressure, p.s.i.a.	10-200	15-100
Rate of introduction of oxidizing agent in s.c.f. (standard cubic feet) per pound of oil per hour.	0.01-3.0	0.04-0.4

Exemplary of the influence of various variables upon the oxidation reaction, it is pointed out that at a temperature of 482° F. and at an air introduction rate of about 0.32 s.c.f. per pound of oil per hour and at about atmospheric pressure, the oxidation reaction requires about 20 hrs. before the desired degree of completion is reached (as measured by increase in viscosity). When the air rate was increased to 1.44 s.c.f. per pound of oil per hour, only 16 hrs. were required to convert the oil to an oxidized product of similar viscosity. Increasing the reaction temperature to 572° F. decreased the time required for oxidation appreciably. Reducing the reaction temperature to below 390° F. increased the reaction time under these conditions.

The time required for the reaction mixture to reach the desired degree of oxidation can be decreased or increased by the use of catalysts. Positive (promoters) or negative (inhibitors) catalysts can be used to modify the reaction rate and time.

Catalysts which have been found to promote the oxidation reaction and to decrease the time required for oxidation reaction include the various well known oxidation catalysts such as the oil soluble salts and compounds containing such metals as copper, iron, cobalt, lead, zinc, cadmium, silver, manganese, chromium, vanadium, and the like, having an atomic number between 51 and 113, inclusive. The naphthenates of these metals are particularly useful. Especially useful and outstanding as a catalyst are those compounds which are obtained by reacting a compound containing both phosphorus and sulfur, such as P_2S_5 , with a terpene, either monocyclic or dicyclic or a mixture thereof, such as pinene as disclosed in my co-pending U.S. application, Serial No. 264,839, filed January 3, 1952. A particularly effective catalyst of this type is widely used as a corrosion inhibitor for petroleum lubricating oils and is sold under the trade name Santolube-395-X, and is a P_2S_5 -terpene reaction product. This reaction product exhibits a marked catalytic effect, resulting in a decrease of several hours in the time normally required for the oxidation reaction to reach the desired degree of completion. Also it is pointed out that the above-mentioned metal naphthenates, especially the copper and iron naphthenates, effectively catalyze the oxidation reaction at a temperature in the range 300° to 500° F. Usually, however, the catalytic effect of these metal naphthenates is pronounced for only a few hours and then becomes ineffective, the addition of more naphthenates being required in order to maintain a catalytic effect upon the oxidation reaction.

Negative catalysts or inhibitors, i.e., materials which tend to increase the time required for the oxidation reaction, are usually high molecular weight aliphatic alcohols such as the C_{16} - C_{24} highly branched, non-straight chain and normal aliphatic alcohols. Typical materials

useful as an anti-catalyst or inhibitor is a highly branched octadecyl alcohol, such as 2,2,4,5,8,10,10-heptamethyl-5-undecanol and n-octadecyl alcohol.

These catalysts can be added in catalytic amounts, usually in the range 0.1 percent to 4.0 percent by weight of the oil undergoing oxidation, depending upon the catalytic promoting or inhibiting effect desired. An amount of one of these types of catalyst, such as about 1.0 percent by weight of the oil is sufficient for most purposes. It is pointed out that the employment of catalysts is beneficial in that they decrease or increase the time required for oxidation (for better control) and in some cases even improve the quality of the detergent recovered as a product from the oxidation reaction. However, the presence of a catalyst, positive or negative, is not essential to the practice of this invention.

More active oxidizing agents, such as sulfur trioxide may also be used in the oxidation step as pointed out above. When liquid sulfur trioxide is utilized as the oxidizing agent, the reaction is most readily carried out when both the oil and sulfur trioxide are separately diluted with a modifying solvent. Solvents which may be utilized in this operation under suitable temperature conditions include liquid sulfur dioxide, hexane, tetrachloroethylene, ethylene dichloride, pyridine, nitrobenzene and dioxane.

Liquid sulfur trioxide is an extremely reactive compound and, if added directly to the oil, will cause excessive charring and violent splattering. It is necessary to moderate this excessive reactivity by dilution with a solvent such as those disclosed above. A molar ratio of solvent to sulfur trioxide of at least about 1:1 appears to be necessary and it is preferred to use a ratio of 2:1 or greater. Dilution of the oil is also very desirable for the reduction of viscosity and to facilitate mixing, but such a dilution is not required. Dilution of the oil may be obtained with some non-reactive solvent other than that utilized for the dilution of the sulfur trioxide. Use of the same diluent, however, simplifies the recovery problem. Gaseous SO_3 may be introduced into the oil directly or mixed with a carrier gas such as air, nitrogen or other inert gas. In the case of gaseous SO_3 an elevated temperature, e.g. 200 to 300° C. may be used.

The extent of oxidation is determined by the ratio of oil to sulfur trioxide. The weight ratio may be varied from 1:1 to 30:1 but is preferably maintained within the range of between 3:1 to 18:1. Ratios from 3:1 to 8:1 are the most desirable. Very low ratios result in the use of excessive amounts of sulfur trioxide without obtaining a corresponding increase in useful product. Very high ratios fail to obtain sufficient oxidation to be economical.

The initial reaction of the sulfur trioxide with oil is almost instantaneous at room temperature or above but reaction continues for extended periods of time, e.g., up to as much as 144 hours or more. At higher temperatures, the time of the slower secondary reactions is shortened to less than 24 hours. The evolution of sulfur dioxide and other gases causes much foaming and the rate of reaction must be controlled sufficiently to permit the capacity of the apparatus to handle the foaming reaction mixture. The time required for reaction may be shortened to as little as three minutes, in which case, secondary reactions do not take place to any great extent. The quality of the product is not materially affected by the length of reaction time or by the absence or occurrence of the secondary reactions.

The temperatures which may generally be utilized in the oxidation reaction, wherein sulfur trioxide is used as the oxidizing agent, range from -40° F. to 400° F., preferably from 70° F. to 200° F. A very short period of time, usually less than three hours, is required for the initial reaction.

After the reaction, the product is treated for the removal of acid and other impurities. Acid is conveniently

removed from the product by water washing. The product is concentrated in the manner discussed later in connection with the product obtained in a process utilizing a less active oxidizing agent.

The detergent produced by sulfur trioxide oxidation is somewhat improved in color by reduction. This is preferably accomplished by treatment in alcohol with lithium hydride or with zinc and hydrochloric acid. Catalytic hydrogenation or chemical reduction may also be used.

The extent to which the oxidation reaction is carried out is dependent upon the selected oil fraction being oxidized and the yield of detergent material desired. If the oil being oxidized contains a relatively low concentration of lower molecular weight hydrocarbons the oil may be oxidized to a considerable extent, up to as high as 75 percent by weight of the oil charged, without any deleterious effects upon the reaction itself or the detergent product. When the aromatic content of the charge stock is low, such as below about 5 percent by weight of carbon atoms in aromatic rings and especially below about 2 percent by weight, the charge stock can be oxidized to a greater extent without any desirable effects or adversely affecting the yield such as may happen when there is an appreciable amount, above about 5 percent by weight of aromatic carbon atoms present therein. In general, the oxidation reaction is carried out until the oxidized oil has increased in viscosity, when expressed in Saybolt Universal seconds (SUS) at 210° F., from 1.5 to 50 fold, preferably from 3 to 10 fold, over that of the originally charged unoxidized oil. When the oxidation reaction is carried out to a 3 to 10 fold increase in viscosity the yield of active ashless detergent recovered from the oxidized oil amounts to about 15 to 50 percent by weight of the original unoxidized oil. Continued oxidation, especially above about 60 percent, tends to produce a certain amount of oil-insoluble oxidized materials which although they do not adversely affect the effectiveness of the oil-soluble detergent, do adversely affect the yield of the desired product. Also since it is often necessary to remove these oil-insoluble oxidized materials, it is desirable therefore not to continue the oxidation reaction beyond that point at which the oil-insoluble materials are produced.

In general, however, the extent to which the selected oil fraction is oxidized is primarily a matter of convenience based on the ease of handling of reactants and reacted (oxidized) materials, yield desired, and recovery and purification steps contemplated in the production of the desired product. Illustrative of this, it has been found that after carrying out the oxidation reaction and the oil and product are separately recovered from the reaction mixture, the recovered oil can be again oxidized to produce an additional product which is at least equal to and often superior in quality and effectiveness as a lubricating oil detergent additive over the first produced product. Also it has been found that after completion of the oxidation reaction and the product recovered (as by propane fractionation of the oxidation reaction mixture), if the recovered product is again oxidized to a hard brittle mass, the reoxidized material has a detergent power or activity, when tested as a lubricating oil additive, by a hereinafter defined test, in a Lauson engine which simulates the well-known, widely accepted L-1 diesel engine test, only slightly less than the product recovered from the initial and first oxidation reaction.

While the viscosity increase measured in SUS at 210° F. has been stated as one way of determining and measuring the extent of the oxidation reaction, it is not the only way. Another way is to measure the amount of water produced during the oxidation reaction. Another method of determining the extent of the reaction is to measure the detergent activity of the oxidation reaction mixture by a spot plate test. Still another method is to determine the amount of propane insoluble material present in the oxidation reaction mixture. When the oxidation reaction

is completed to the extent desired, the propane insoluble, oil soluble material in the reaction mixture amounts to between about 5 and about 60 percent by weight of the reaction mixture, more often between about 15 and about 40 percent by weight. At low yields of propane insoluble materials below about 5 to 20 percent, it is often difficult to recover the desired product (propane insoluble, oil soluble material) from the reaction mixture.

The oxidation reaction mixture, after oxidation, can be used as an oil additive directly without additional concentration or purification. However, if a product of improved quality, purity and greater concentration and effectiveness per unit weight is desired, the active detergent oil-additive material is preferably removed and recovered from the oxidation reaction mixture. When the hydrocarbon feed to the oxidation reaction is a liquid, the recovery and concentration of the active additive material is preferably obtained by propane fractionation such as is disclosed by J. M. Whitely and G. A. Beiswenger in U.S. Patent 2,110,845.

The active detergent, or dispersant, is actually a firm, plastic or slightly brittle mass soluble in pentane, benzene, diethyl ether and the other usual liquid hydrocarbon solvents. It is also soluble in all petroleum lubricating oils as well as polymers and diester synthetic oils. The additive leaves a dark red color when rubbed on a white surface and when dissolved in a lubricating oil, such as a motor oil, gives the oil a black appearance by reflected light. The additive material has a strong tinting power when dissolved in lubricating oil. The detergent produced by the oxidation of a selected lubricating oil fraction comprises compounds of varying molecular weight, such as oil-like compounds resembling the unoxidized oil of the oxidation reaction mixture to hard brittle oxygen-containing compounds, the molecular weight of which is many times greater than the molecular weight of original unoxidized oil. The solid detergent product has a low acid number below about 50, expressed as the number of milligrams of KOH per gram, a saponification number between 0 and about 100. The oxygen content of these materials range from about 2 percent up to about 10 percent by weight, usually from 3 percent to 8 percent, although in some cases the oxygen content may be as high as 15 percent or as low as 1 percent by weight.

While these solid oxygen-containing materials which are very effective as detergents in lubricating oil compositions appear to have a superficial resemblance to resins, asphaltenes and sludges heretofore reported in the literature, there are a number of distinct and fundamental differences thereover. These materials such as sludges, asphaltenes and resins are characterized by insolubility in light hydrocarbons, have a high acid number, in some cases as high as 180 and also possess high saponification values, usually above 300 and even as high as 450. In contrast thereto, the materials of the invention of copending application Serial No. 304,659, are soluble in light hydrocarbons, have an acid number below about 50 and a saponification number below about 100.

The active ashless detergent material of the invention of Serial No. 304,659, produced during the oxidation reaction, dissolves in the lubricating oil from which it is prepared since it is oil soluble. As indicated hereinbefore, the oxidized reaction mixture itself is useful as a lubricating oil additive since it possesses detergent properties when added to or compounded with a lubricating oil. Since the active detergent in the oxidized reaction mixture is diluted with a considerable amount of the original, unoxidized lubricating oil as a solvent therefor, a considerable amount of the oxidized reaction mixture must be added to a lubricating oil before it imparts effective detergent action thereto. Accordingly if the oxidized reaction mixture is added directly to a petroleum lubricating oil to impart detergent properties thereto, the amount of added oxidized reaction mixture added thereto usually comprises between about 5 and 75 percent by weight

usually between about 20 and 50 percent by weight of the total admixture.

It is often desirable to prepare a concentrate of the active solid detergent material which comprises substantially only the solid detergent material. This active solid detergent material can be recovered directly from the oxidized reaction mixture by solvent extraction with a solvent which is selective for the relatively unoxidized, essentially hydrocarbon material therein and which solvent is at the same time essentially a non-solvent for the active detergent material in the reaction mixture. Suitable solvents for the recovery of the solid active detergent material from the oxidized reaction mixture include propane, isopropyl alcohol, a solvent mixture of propane with modifying amounts (up to about 50 percent by weight) of other low boiling hydrocarbons such as methane, ethane, and butane. Other selective solvents such as methyl ethyl ketone, methyl isobutyl ketone, tertiary butyl alcohol, isobutyl alcohol, ethyl acetate, dioxane, morpholine, dimethyl formamide, phenol and isopropyl alcohol are also useful. In general those polar compounds containing only carbon, hydrogen, and oxygen atoms, such as aliphatic alcohols, aliphatic ketones, and esters having from 3 to 8 carbon atoms per molecule are useful as treating materials in the practice of this invention. Mixtures of these various materials may be used.

One step-wise process for concentrating the detergent material comprises extracting the partially oxidized oil with methyl isobutyl ketone, methyl ethyl ketone or mixtures of the two at appropriate temperatures so as to dissolve only the oil and lower molecular weight oxidation material. The proper temperature will depend upon the ratio of solvents and the percentage of product to be dissolved. The undissolved material is thereafter mechanically separated from the dissolved material.

When these materials are used in obtaining the active detergent material from the oxidized reaction mixture, the active solid detergent is recovered as a propane insoluble, oil soluble, solid phase (raffinate), the ineffective, substantially hydrocarbon material of the reaction mixture being dissolved in the treating material as an extract. The propane soluble phase from which the active detergent material is separated has a viscosity index much higher than that of the unoxidized oil. This propane soluble phase may be used to blend with an oil for the purpose of improving the viscosity index of that oil.

In the recovery of the active detergent material, it is preferred to employ propane as a selective solvent, the solid active detergent being recovered as a separate propane insoluble phase under propane fractionating conditions of temperature, pressure and ratio of solvent to material being treated (usually 5:1 to 25:1 by vol.). The solvent extraction operation for the recovery of the active detergent material is usually carried on at a temperature in the range 50° F. to 250° F. especially in the range 100° F. to 160° F. and a pressure of between 200 p.s.i.g. to 500 p.s.i.g. Countercurrent solvent extraction techniques are usefully employed as well as multiple, solvent extraction steps of separately contacting and recovery of the undissolved active detergent.

In many instances, the activity of the detergent material is considerably increased by additionally treating this recovered solid detergent material with an aliphatic alcohol, in the C₃ to C₈ range, such as isopropyl alcohol, and recovering a purified and more active detergent therefrom as a solid, alcohol insoluble phase. The alcohol treatment has a two-fold purpose. Traces of peroxides, aldehydes, and the like which may be oxidation promoters are removed thereby. In addition thereto, it appears that a beneficial chemical change takes place during stripping of residual alcohol solvent from the additive material.

The above-described sequence of recovery and purification steps does not in some instances greatly influence the quality and effectiveness of the solid, final detergent

product. It is preferred to employ a propane fractionation step prior to the organic polar compound treating step to avoid emulsions which are difficult to break and which present operational difficulties when the alcohol or ketone treating step precedes the propane solvent extraction step.

The oil to which the solid active detergent material is added can be any oil of lubricating viscosity and preferably is a lubricating oil commonly used in internal combustion engines, such as in the crankcase thereof. The additive is usually added to the base lubricating oil in effective detergent amounts and generally comprises between 0.1 percent to 10 percent by weight of the total lubricating oil composition but may be as high as 25 percent for extreme service conditions. Usually, however, an amount in the range 0.3 percent to 5.0 percent by weight of the total lubricating oil composition is sufficient.

There may also be added to the lubricating oil compositions including the detergent, other oil additives which are usually present in lubricating oil compositions. These additives may include corrosion inhibitors, oxidation inhibitors, viscosity index improvers, pour point depressants, extreme pressure additives, peptizing or dispersing agents, lubricity agents and the like. However, since the detergent material, when employed in lubricating oil compositions is an ashless detergent, it would obviously be appropriate to employ only those other additives which are also ashless. However, even when the other additives present in the lubricating oil composition are not ashless, the use of the subject ashless detergent additive would yield an oil of lower ash content than otherwise if a detergent other than an ashless detergent were employed.

Each of the following objects will be attained by at least one of the aspects of this invention.

It is an object of this invention to produce an improved lubricating oil composition.

It is another object to provide an improved method for preparing an ashless detergent for lubricating oils.

It is another object of this invention to provide an improved method for preparing a detergent composition from petroleum.

It is still another object to provide a method for oxidizing a lubricating oil fraction with nitric acid so as to produce an ashless detergent material.

Other objects and advantages will be apparent to those skilled in the art upon study of the accompanying disclosure.

I have discovered that selected lubricating oil fractions can be oxidized by reaction with nitric acid so as to produce an improved ashless detergent material. I have discovered that such lubricating oil fractions can be reacted with dilute nitric acid, at relatively low temperatures and at atmospheric pressure, so as to produce a reaction product, which upon being heated to a relatively high temperature, is converted into an ashless detergent material. I have also discovered that such lubricating oils can be oxidized by concentrated nitric acid at a temperature of 400° F. or above in a one step process to produce the detergent composition of this invention. It is also possible to oxidize a selected lubricating oil fraction with dilute nitric acid at a temperature of 400° F. or above so as to produce the detergent material in a single step provided an elevated pressure is employed. The pressure required will be determined by the vapor pressure of the aqueous nitric acid solution utilized.

The detergent materials prepared according to the process of this invention are substantially acid-free and do not exhibit high corrosive tendencies when used as additives for lubricating oils although it is generally preferable to incorporate a corrosion inhibitor along with the detergent material in a lubricating oil.

I have found that nitric acid will perform the oxidiz-

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ing reaction upon lubricating oils at substantially lower temperatures than are possible with other oxides of nitrogen. Thus dilute nitric acid containing from 10 to 50 weight percent of HNO_3 can be reacted with lubricating oil fraction for a period of 1 minute to 30 hours or longer at a temperature of from room temperature to 200° F. The product so obtained can then be converted into detergent material by heating for a period of 1 to 30 minutes at a temperature of 400 to 600° F. I have found that the material has been converted into a detergent upon being heated to a temperature of 480° F. and thereafter immediately cooled.

Conditions which are satisfactory for producing the ashless detergent by the process of this invention utilizing dilute nitric acid, from a selected hydrocarbon fraction, are given in the following Table I.

TABLE I

Reaction Conditions	Broad Range	Preferred Range
Oxidation Temperature, ° F.....	room temp.-200.....	140-170.....
Time of Oxidation.....	1 min. to 30 hrs.....	4-10 hours.....
Pressure.....	10-50 p.s.i.a.....	atmospheric.....
Conc. of HNO_3 acid, wt. percent.....	10-50.....	25-40.....
Heating temp. after oxidation, ° F.....	400-600.....	435-575.....
Time of heating after oxidation, Min.....	1-30.....	5-10.....

When concentrated nitric acid is used as the oxidizing agent, and the one-step process is utilized, the acid is emulsified with the lubricating oil and the emulsion is heated to a temperature of 400° F. or above so as to produce the detergent composition. One means to accomplish this heating step is to spray the emulsion onto a surface maintained at 400° F. or above, allowing the material to drain from the surface, and collecting the material. A satisfactory surface is a pipe; the pipe may be conveniently heated by any conventional means from the outside, and the acid-oil mixture sprayed onto the inner walls of the pipe. This method is convenient for the short reaction times which are preferably utilized. No additional heat treatment is required in this case because the temperatures employed are sufficiently high so that the additional heating step is not required. Conditions which are generally satisfactory for producing the ashless detergent from a selected hydrocarbon fraction, using concentrated nitric acid, in the one-step process, are given in the following Table II.

TABLE II

Reaction Conditions	Broad Range	Preferred Range
Oxidation Temperature, ° F.....	400-600.....	475-575.....
Reaction Time.....	1 sec.-5 min.....	1-2 min.....
Pressure.....	10-50 p.s.i.a.....	atmospheric.....
Acid Concentration, wt. percent HNO_3	60-100.....	20 p.s.i.a. 65-80.....

Materials which are suitable for producing the ashless detergent of this invention include those materials disclosed and claimed in copending application Serial No. 304,659, and hereinbefore set forth and described with reference to that application. In addition to the materials hereinbefore set forth, lubricating oils having a SUS viscosity of as low as 58 at 210° F. can be utilized.

The following examples illustrate the invention but are not to be construed as limiting the invention. In the examples, reference is made to the following test procedures.

The carbon spot test referred to hereinafter in the examples comprises the steps of utilizing a standard mixture of oil and corrosion inhibitor in normal concentration plus 0.4 weight percent carbon black. For one measured

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drop of this mixture the carbon black spreads to a circle of 16 millimeters in diameter on a flat polished steel plate which is maintained at 482° F. The test mixture which is utilized in the example is the above identified standard mixture plus a designated percent of detergent product. Any increase in diameter over 16 millimeters of the carbon spot resulting on the flat polished steel plate is an indication of improvement provided by the detergent action of the detergent additives.

The simulated L-1 Lauson engine test used in connection with the following examples is described in "Motor Oils and Engine Lubrication," by Carl W. Georgi, at page 683 and following. The operating conditions which were utilized in the tests of the following examples have been modified and are as follows:

The lubricating oil employed as a base oil in these tests was a solvent-refined Mid-Continent oil of lubricating viscosity and having the following characteristics

20 Gravity API.....	30.3
Viscosity at 210° F., SUS.....	61.8
Viscosity index.....	98
Neutralization number.....	0.01

The ashless detergent in selected amounts was added to the base oil and tested in a standard Lauson engine. The test consisted in placing 920 gms. of the base oil containing this ashless detergent in the crankcase of a single cylinder Lauson gasoline engine. The engine was operated under a 1.2 horsepower load at 1600±20 r.p.m., maintaining a cooling jacket temperature of 300° F., an oil temperature of 225° F., an air-to-fuel ratio of 13.5:1, carburetor air at room temperature, spark advance of 25° B.T.D.C., and crankcase vacuum of 1.0 inch of mercury. At the end of 60 hours' engine operation under these conditions the engine was stopped, disassembled, and the piston, crankcase and bearings were examined. The piston varnish was rated on an arbitrary scale of 0 to 10 with 10 representing a clean or perfect condition and 0 representing the dirtiest condition.

EXAMPLE I

A base feed stock was prepared from a Mid-Continent crude oil by propane fractionation and solvent extraction having the following properties: viscosity of 4278 SUS at 100° F., viscosity of 203 SUS at 210° F., and a viscosity index of 93. Substantially equal volumes of the above lubricating oil stock and aqueous nitric acid containing approximately 35 weight percent nitric acid, prepared by adding one volume of water to one volume of approximately 70 weight percent HNO_3 , were heated to the boiling point of the nitric acid which was approximately 165° F. and heating was continued under reflux for a predetermined time in a series of runs. A similar run was made utilizing aqueous nitric acid containing about 25 weight percent nitric acid. At the end of the reaction period the acid layer was removed and the oil washed with water. The oil was then dissolved in n-pentane containing isopropyl alcohol. The oil-pentane layer was then washed with a solution of equal volumes of isopropyl alcohol and water. The pentane was then removed by evaporation leaving a red oily substance as the product of the reaction. This material showed no detergency when tested by the spot plate method. The material after heating was converted into a black oil which was found to have good detergency as evidenced by the spot plate test. The products obtained from several different runs were tested by the Lauson engine method, described above. The runs were conducted utilizing 3.5 weight percent of detergent in the base oil along with 0.82 weight percent of a commercial corrosion inhibitor prepared from the reaction product of phosphorus pentasulfide and a terpene. The results of the Lauson engine test are shown in Table III.

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TABLE III

Nitric Acid Concentration	Reaction Time	Piston Varnish Rating
35 wt. percent.....	5 minutes.....	8.2
35 wt. percent.....	4 hours.....	9.2
35 wt. percent.....	12 hours.....	16.5
17.5 wt. percent.....	8 hours.....	8.2
0.....	0.....	6.2

¹ This additive was not heated to 480° F.

EXAMPLE II

A sample of the paraffinic lubricating oil feed stock described in Example I was reacted with an equal volume of aqueous nitric acid containing approximately 35 weight percent HNO₃ by heating the reactants to the boiling point of the nitric acid, which was approximately 165° F. The reaction was continued for about 4 hours at this temperature.

The resulting oxidized oil was distilled in a molecular still. Molecular distillation consists of heating a liquid, usually spread in a thin film or layer, which has in close proximity to the surface of feed liquid a cooler condensing surface and keeping the intervening space evacuated to such a degree that the mean free path of the evaporating molecules is greater than the distance between the surface of the evaporating material and the condenser. Molecular stills are known in the art and an improved molecular still is described in U.S. Patent 2,585,202, issued 1952 to W. B. Whitney. The results of the molecular distillation are tabulated in Table IV.

TABLE IV

Cut No.	Pressure, mm. of Hg	° F.	Wt. Percent	Cumulative, Wt. Percent	RI@25° C.	Carbon Spot Test	
						Before Heating to 480° F.	After Heating to 480° F.
1.....	10-20	311-320	2.4	2.4	1.4848	20	27
2.....	20	356-365	5.6	8.0	1.4900	19	21
3.....	20	365-392	10.3	18.3	1.4931	-----	-----
4.....	20	392-397	2.4	20.7	1.4932	12	24
5.....	15-20	419-437	3.1	23.8	1.4935	-----	-----
6.....	15-20	442	2.3	26.1	1.4937	-----	-----
7.....	15-20	473	4.5	30.6	1.4963	-----	-----
8.....	15	446-500	3.0	33.6	1.4962	17	21
9.....	15	440-464	2.0	35.6	1.4965	-----	-----
10.....	15	440-464	5.8	41.4	1.4970	-----	-----
BTMS.....	-----	-----	53.7	95.1	1.5079	42	42
Loss.....	-----	-----	-----	4.9	(very dark)	-----	-----
Base Oil.....	-----	-----	-----	-----	-----	-----	-----

The products obtained by the molecular distillation were examined by infrared spectroscopy. The results of the infrared spectroscopy are shown in Table V.

TABLE V
Infrared data

Absorption Band Wave Length, Microns	Probable Origin	Cut #1	Composite of Cut #3, 4, 5, 6	Intensity 1—Composite of Cut #7, 8, 9, 10	Bottoms
5.78-5.83.....	C=O	.79.....	.47	.57.....	.6.
5.70.....	C=O	.77.....	.40	.25.....	absent.
6.20.....	C=C Arom.	.37.....	.76	1.09.....	1.64.
6.40.....	N=O	.87.....	.64	small.....	very small.
6.52.....	N=O	very small.....	.41	.65.....	1.24.

¹ The numbers for a given absorption band (horizontal lines) indicate the relative concentration of the functional groups responsible for this absorption band. The numbers in the vertical columns indicate the relative absorptivities at the respective wave lengths but due to the different absorption intensities of the various groups, these numbers do not indicate variations in concentrations.

The results of the infrared spectroscopy show that the products obtained by oxidation of the lubricating oil fraction with nitric acid differ from air oxidized products

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in the bands reported at 6.40 and 6.52. These bands do not appear in the air oxidized product and have been tentatively identified as due to nitro groups. These bands also appear in the analysis of lubricating oil fractions oxidized by the dilute acid method both before and after the subsequent heat treatment. The heated material differs from the unheated material primarily in a slight reduction in the nitro groups.

EXAMPLE III

A sample of the paraffinic lubricating oil feed stock described in Example I was emulsified with 6 weight percent of nitric acid containing 70 weight percent HNO₃ and was then passed through a tube heated to 480° F. at a rate so as to provide a residence time of 1 to 2 minutes. The heat was supplied by an electrical resistance wire wrapped around the tube and the temperature was controlled by a thermocouple immersed in the emulsion flowing through the tube.

The oxidized oil obtained was then dissolved in methyl isobutyl ketone. Acetone was added and the acetone insoluble product which precipitated was recovered and tested for viscosity and detergent properties. The viscosity was 322 SUS at 210° F. and the results of the carbon spot test was 46 mm. as compared to 16 mm. for the base oil.

EXAMPLE V

Several runs were made using concentrated nitric acid in different amounts in the oil as the oxidizing agent. The oil used in these runs was the same as that used in the foregoing examples. In each case the acid was

mixed with the oil so as to form an emulsion and the emulsion was charged to the heated tube so as to provide a residence time of 1 to 2 minutes. In each case

the oxidized oil was propane fractionated and the propane insoluble fraction obtained was tested for detergent properties by the carbon spot test. The propane frac-

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tionation was conducted in a continuous counterflow column utilizing 6.88 volumes of propane per volume of oil. The top column temperature was 153° F. and the bottom column temperature was 148° F. The results of these tests are shown in Table VI. The amount of acid reacted with oil in each case is based on the amount of 70 to 71 weight percent nitric acid.

TABLE VI

The effect of varying the amount of concentrated nitric acid used to oxidize a lubricating oil fraction

Wt. Percent of 70 to 71 Assay Nitric Acid	Residence Time, minutes	Temp., ° F.	Carbon Spot Test
0 (Base Oil).....	1 to 2	480	16
1.0.....	1 to 2	480	24
1.0.....	1 to 2	480	27
2.0.....	1 to 2	480	24
2.0.....	1 to 2	480	25
6.0.....	1 to 2	480	27
6.3.....	1 to 2	480	28
8.8.....	1 to 2	480	29
11.8.....	1 to 2	480	27
14.8.....	1 to 2	480	28

The above runs demonstrate that the amount of concentrated acid employed in the oxidation reaction can be varied within wide limits without appreciable effect upon the product produced.

EXAMPLE V

Samples of the refined lubricating oil fraction utilized in the previous examples was reacted for several hours with N₂O, NO and NO₂ at a temperature of 160° F. There was substantially no increase in viscosity, no water formation and no evidence of detergency on the part of any of the treated samples.

The nitric acid treated oil has a lower viscosity than that of air treated oil, the nitric acid oxidized oil having a viscosity of 384 SUS at 210° F. compared to 600 SUS at 210° F. for air oxidized oil. The average molecular weight of nitric acid oxidized oil is apparently much less than oil air oxidized to only 300 SUS at 210° F. because such air oxidized oil yields 12 to 15 weight percent bottoms upon propane fractionation whereas 384 SUS at 210° F. nitric acid oxidized oil yields only about 1.4 weight percent bottoms upon a similar propane fractionation.

Although two processes are described for the nitric acid oxidation of the selected lubricating oil stocks, the end results of both are essentially the same because the product of the reaction, in either case, must be heated to a temperature of 400 to 600° F. in order to produce the detergent composition of the invention. It is usually economically advantageous to carry out the reaction at atmospheric or near atmospheric pressure and this can be done at a temperature of 400° F. or above if concentrated nitric acid is used but if dilute nitric acid is used, the boiling temperature of the dilute acid sets the upper temperature limit at atmospheric pressure. Thus dilute nitric acid can be used to produce the detergent

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material in a single step provided the reaction is conducted under sufficient pressure so as to permit a temperature of 400° F. or above. Similarly concentrated acid can be used to oxidize the oil at a relatively low temperature, such as 160° F., and the reaction product then heated to 400 to 600° F. to produce the detergent material.

That which is claimed is:

1. A process for producing a material having detergent and dispersant properties which comprises subjecting a propane-fractionated, solvent-extracted hydrocarbon fraction containing at least 40 carbon atoms per molecule and having a viscosity of at least 58 SUS at 210° F. to oxidation in the presence of nitric acid containing from 10 to 50 weight percent HNO₃ at a pressure of 10 to 50 p.s.i.a. and a temperature of from room temperature to 200° F. for a period of time in the range of 1 minute to 30 hours; and subjecting the resulting reaction product to a temperature in the range of 400 to 600° F. for a period of time in the range of 1 to 30 minutes.

2. A process for producing a material having detergent and dispersant properties which comprises subjecting a propane-fractionated, solvent-extracted hydrocarbon fraction containing at least 40 carbon atoms per molecule and having a viscosity of at least 58 SUS at 210° F. to oxidation in the presence of nitric acid containing from 25 to 40 weight percent HNO₃ at the boiling point of the acid for a period of time in the range of 4 to 10 hours; and subjecting the product obtained to a temperature in the range of 435 to 475° F. for a period of time in the range of 5 to 10 minutes.

3. A process for producing and recovering a material having detergent and dispersant properties which comprises subjecting a propane-fractionated, solvent-extracted hydrocarbon fraction containing at least 40 carbon atoms per molecule and having a viscosity of at least 58 SUS at 210° F. to oxidation in the presence of nitric acid containing from 10 to 50 weight percent HNO₃ at a pressure of 10 to 50 p.s.i.a. and a temperature of from room temperature to 200° F. for a period of time in the range of 1 minute to 30 hours; subjecting the reaction product to a temperature in the range of 400 to 600° F. for a period of time in the range of 1 to 30 minutes; removing remaining nitric acid from the reaction product; treating the reaction product with sufficient liquid propane to dissolve unreacted oil; and recovering the propane insoluble detergent material as the product of the process.

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