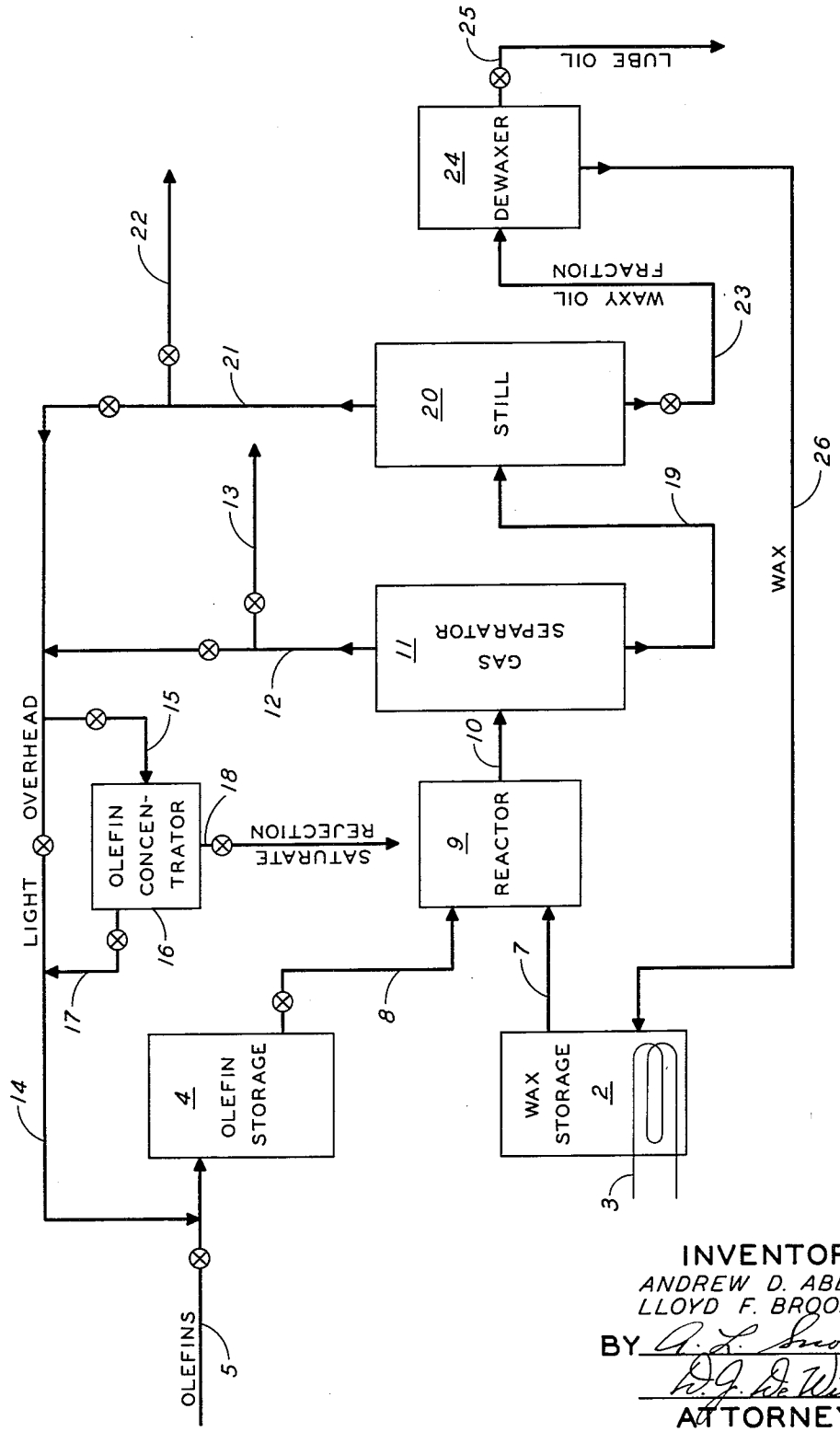
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LUBRICATING OIL AND PROCESS FOR FORMING THE SAME

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LUBRICATING OIL AND PROCESS FOR FORMING THE SAME

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This application relates to the provision of a novel lubricating oil and a process for producing this oil. More particularly, the invention concerns a process wherein hydrocarbon waxes petroleum or other origin are reacted with olefins, especially ethylene, to produce a lubricating oil of outstanding characteristics. This application is a continuation-in-part of our copending applications, Serial Nos. 281,446 and 281,447, both filed April 9, 1952, and now abandoned.

It has long been recognized that hydrocarbon waxes have good lubricating qualities as long as they are maintained in the molten condition. Thus, such waxes have good lubricity, a high viscosity index, and good stability. On the other hand, it is obvious that waxes can have but a limited utility as lubricating oils due to their high melting, or pour point. If this deficiency of waxes could be overcome, the resulting liquid products would receive serious consideration for many lubricating applications since the waxes themselves are available in a wide range of viscosities. Accordingly, it is an object of the present invention to provide a treatment whereby hydrocarbon waxes are so altered in structure as to effect a major reduction in their melting point while at the same time preserving the desirable lubricating, stability, viscosity and viscosity index qualities of the wax.

While attainment of the foregoing object has the effect of providing the art with a novel lubricating oil, the synthetic oil art has now progressed to the point where no such oil can meet with general commercial acceptance unless it possesses truly outstanding and unique characteristics. This is particularly the case with synthetic oils proposed for use as crankcase lubricants in automotive or other internal combustion engines since such oils are considerably more costly than natural petroleum oils and must justify the added expenditure. Experience in the field shows that a successful synthetic crankcase oil, in addition to having excellent lubricating and viscosity characteristics, should also be fully compatible with and respond well to treatment by, the various additives such as anti-oxidants, detergents, corrosion inhibiting agents, blooming agents, and the like which now are conventionally incorporated in crankcase lubricating oils. It is also important that the synthetic oil be compatible in all proportions with natural mineral oils. This is a factor of considerable importance from the practical standpoint, for not only does it permit the marketing of a variety of blends, each of which is particularly well adapted for a given climatic or other condition of usage, but it also permits the operator of the vehicle to replenish the main body of synthetic oil in the crankcase with a conventional oil, if need be, without danger of forming an incompatible mixture in the crankcase. While a number of different synthetic oils are now available, none fulfills all these desirable attributes, and it is therefore a further object of this invention to provide from waxy hydrocarbons a novel synthetic oil of satisfactory pour point characteristics which couples good lubricating, viscosity and viscosity index qualities with a high degree of compatibility with mineral oils and with the various oil additives, and which responds well to treatment by said additives.

Another important quality of an automotive crankcase lubricant relates to the amount of deposit which the oil leaves in the combustion chamber as the engine is operated. Such combustion chamber deposits, whether attributable to the oil or to the fuel, have the effect of increasing the octane requirement of the engine. Due to the added costs of premium fuels, it is desirable to keep this octane requirement increase as low as possible even in the case of those engines having a relatively low initial octane requirement. The problem becomes even more serious with many of the modern high compression engines which require the use of premium fuels even when the motor is clean. Accordingly, it is a highly important object of this invention to provide a lubricating oil which not only possesses the desirable compatibility and other characteristics outlined above, but which also has outstandingly low deposit-forming characteristics when employed as the crankcase lubricant in an automotive or other internal combustion engine.

The nature of still other objects of this invention will appear as the description thereof proceeds.

We have now discovered that the foregoing objects are attained by reacting a hydrocarbon wax, or mixture of said waxes, with one or more olefin compounds, and preferably with ethylene. This reaction, which is conducted under elevated conditions of temperature and pressure, proceeds to a certain extent even in the absence of a catalyst, though it is greatly speeded up and the nature of the product oil improved by using chloroform, methylene chloride or other alkyl halide as the catalyst.

The oils which can be obtained in this fashion have relatively low pour points, good lubricity and a high viscosity index. They are available in a wide range of viscosities and hence are adapted to be employed as crankcase lubricants in automotive engines, as well as for other lubricating purposes. They are compatible with mineral oils in all proportions and at any desired temperature, and blends of outstanding quality have been prepared. They are also fully compatible, when employed either alone or in a mineral oil blend, with the various oil additives, and they respond well to treatment by said additives. In these as well as other particulars, the present oils are far superior to other types of synthetic oils which are presently available on the market.

The oils of the present invention are also characterized by abnormally low deposit-forming characteristics when employed as crankcase lubricants in internal combustion engines. In consequence, the use of said oils (or of mineral oil blends containing substantial amounts of the present oils) in a clean engine has the effect of establishing a lower ultimate octane requirement than is the case when a conventional mineral oil is employed alone, the same fuel being used in both cases. While the present oils thus make for improved engine performance by reducing engine deposits, it should also be noted that the high viscosity index of these oils makes it possible to employ a much lighter grade thereof than would otherwise be practical and thereby effect a significant reduction in frictional losses as compared with those experienced when a heavier grade of oil is used. Any such reduction in frictional loss is accompanied by a corresponding increase in the mileage obtained with any given fuel.

The waxy compound, or mixture of such compounds, to be reacted with the olefin can be any hydrocarbon of predominantly open-chain configuration which contains from about 15 to 100 carbon atoms in the molecule, and which is substantially free of aliphatic unsaturation. Included are various members of the paraffin series of hydrocarbons such as pentadecane, hexadecane (cetane), 2-

methylheptadecane, 4-propylnonadecane, eicosane, pentacosane, octacosane, triacontane, tritetracontane, heptacontane and the like, as well as hydrocarbon compounds containing a long hydrocarbon chain such as dodecylcyclohexane, octadecylbenzene, 2-octadecyldecalin, and tetradecylcyclopentane. Also included are various crystalline and micro-crystalline paraffin waxes, including slack and petrolatum waxes and wax mixtures, ceresin, ozokarite and polyethylene waxes as well as those derived from the Fischer-Tropsch synthesis or by the destructive or non-destructive hydrogenation of synthetic hydrocarbons, coal, shale oil or the like. These waxes, many of which are made up of a mixture of various hydrocarbon compounds and which frequently contain small percentages of other, non-paraffinic compounds such as naphthenes and the like, can be employed either in the form in which they are recovered, or they can first be separated into particular compounds, fractions, or mixtures of such compounds or fractions, with the separated component(s) then being reacted with olefin to form the oils of the present invention. Of the available hydrocarbon wax reactants, a preferred class for the purpose of this invention is made up of the various crystalline and micro-crystalline waves which are recovered from petroleum oils; these paraffin waxes consist essentially of saturated, open-chain hydrocarbons having from about 20 to 40 carbon atoms in the molecule and melt above 70° F. when free of oil.

As the olefin reactant there can be employed any mono-olefin containing from 2 to about 10 carbon atoms in the molecule, these compounds being employed either singly or in any desired admixture. Most advantageously employed in accordance with the invention are the normally gaseous mono-olefins such as ethylene, propylene, butene-1, butene-2, and isobutene. Mixtures of these gases are conveniently obtained as off-take streams from various petroleum refining processes, and such mixtures can be employed directly, if desired. Ethylene, whether employed alone or as the principal constituent of a gaseous mixture, constitutes the most preferred olefinic reactant. Other examples of olefinic reactants which can be employed in this invention are pentene-1; pentene-2; 2-methylbutene-1; cyclopentene, cyclohexene, 3-methylbutene-1; 2-methylbutene-2; hexene-1; 3-methylpentene-2; heptene-1; octene-1; octene-2; decene-1; and decene-2.

As indicated above, the present reaction proceeds in the most favorable manner in the presence of a catalyst, and a suitable material of this class is therefore preferably employed. The only compounds which have been demonstrated to have a beneficial catalytic action in the process of this invention are the hydrocarbyl halides, and more particularly the alkyl halides. Included within this term are such compounds as chloroform, methylene chloride, methyl chloride, carbon tetrachloride, tetrachloroethane, dichloropropane, butyl chloride, chlorinated naphthas, methylene fluoride, propyl bromide, octyl iodide, dichloro-monofluoromethane, and the like.

In carrying out the reaction of olefin and wax, there is employed from about 1 to 25 moles of the olefin per mole of wax. A preferred reactant ratio, however, is from about 2 to 10 moles of olefin per mole of wax. The amount of catalyst to be employed will vary somewhat depending on the nature of the reactants, as well as upon the particular catalyst material, or mixture of said materials, which is used. In general, good results have been obtained by using from 0.1 to 10% by weight of the catalyst, while a preferred range is from 1 to 5% by weight, both of these percentages being based on the weight of wax charged.

The reaction of the present invention is carried out, under the elevated conditions of temperature and pressure discussed below, by bringing the olefin into reactive engagement with the wax reactant as the latter is maintained in the liquid condition; as aforesaid, a catalyst is preferably present in the reaction mixture also. The wax may be placed in the liquid condition by melting the same or by employing a solution of the wax in a solvent which is relatively inert under the conditions of the reaction. The solvent can, if desired, be a petroleum oil or a suitable portion thereof. Thus, many petroleum crudes, lubricating oils, gas oils or fuel oils which contain an appreciable percentage of wax are difficult to work because of their high pour points. The Minas and Ute Tribal crudes, having pour points in some instances as high as 95° F., are exemplary of such products. These crudes, or wax-containing distillates or residues obtained therefrom, can be reacted with an olefin in accordance with the process of this invention, with the result that a substantial portion of the wax present therein is converted to a lubricating oil of low pour point. This not only improves the yield of lubricating oil from the starting material, but also so decreases the pour point of said material as to greatly facilitate the handling and refining thereof. When this procedure is adopted, the wax-olefin oil produced is normally left with the other oil as the resulting oil blend has excellent over-all properties.

The reaction between the olefin and the wax proceeds at temperatures of from about 400 to about 700° F. Superatmospheric pressures are employed, primarily to promote the solution of the olefin reactant in the liquid wax material and to maintain the other components of the system in a liquid condition at the elevated temperatures employed. While any pressure between about 100 and 15,000 p. s. i. g. can be employed, pressures between about 1,000 and 4,000 p. s. i. g. are preferred. This pressure is normally supplied in large part by the addition of a gaseous olefin reactant, though nitrogen, carbon dioxide, ethane or other inert gases can also be employed for this purpose. In such cases, the olefin can be supplied in liquid form, if desired, when physically possible.

In carrying out the process of this invention, a number of competing reactions take place, and it is thought that a proper understanding of these reactions is essential to an intelligent expression of the preferred reaction conditions and operating procedures to be employed. The predominant reaction is believed to be one wherein the wax is alkylated by the olefin; thus, in the case of ethylene, a given wax molecule would acquire at least one, and usually more than one, ethyl side chain. Polymerization of the olefin reactant also plays a significant, though minor role in the reaction, while a third reaction (which normally takes place in very small degree) involves the cracking of the waxy starting material or the alkylated wax product. The cracking reaction is a particularly deleterious one, for if it occurs to any appreciable extent the deposit-forming and additive-responsive qualities of the final oil product are seriously impaired. Fortunately, it has now been found that the cracking reaction can be substantially eliminated by maintaining the reaction temperature below about 700° F. While temperatures between 700 and 800° F. would otherwise be desirable since they have the effect of speeding up the desired alkylation reaction, such temperatures cannot be employed for more than relatively short periods of time if cracking of the wax is to be avoided. On the other hand, temperatures above 600° F. are preferably employed wherever possible so as to speed the reaction as much as possible without otherwise adversely affecting the course thereof. The olefin polymerization reaction is also undesirable, though to a lesser extent than is the case with the cracking reaction. We have found that the olefin polymerization reaction can be minimized by gradually adding the olefin to the heated wax as the reaction progresses, the addition of olefin being made in a continuous or intermittent fashion, as more particularly described below. Accordingly, in the preferred practice of this invention, reaction temperatures between 600 and 700° F. are employed, and the olefin is added to the heated reaction mixture (preferably along with catalyst) as the reaction progresses.

As indicated above, the reaction time will vary depending on the temperature employed. It also varies with the

nature of the olefin reactant and the relative rate at which the olefin is admitted to the reaction zone. Thus, ethylene is much more reactive than the other olefins and requires a shorter reaction period. As a general rule, however, good results are obtained using reaction periods of from 1 to 20 hours, and in some cases, appreciable reaction will occur in even shorter periods, particularly with ethylene.

As will occur to those skilled in the art, the reaction may be carried out batchwise, as in an autoclave, semi-continuously or continuously, as in a tube reactor. The olefin, moreover, may be charged to the reaction zone all at one time or in portions. The pressure in the reaction zone may be maintained by the olefin alone or, as indicated above, an inert gas may be used in aiding maintenance of the desired pressure. The reaction is essentially a liquid phase reaction; that is, reaction occurs between liquid wax and olefin dissolved therein. Accordingly, agitation of the reaction mixture will be found advantageous. Moreover, it is often desirable to avoid too high a concentration of olefin in order to discourage competing reactions, such as the polymerization of the olefin. Therefore, in order to encourage the preferential reaction of addition of olefin to wax and to ensure a more uniform distribution of olefin on the wax molecules, the olefin preferably is gradually charged to the reaction zone as the reaction progresses. In operating batchwise, this can conveniently be accomplished by adding the olefin to the reaction vessel in successive increments, each of the order of about 5 to 40 per cent of the total olefin charge. After all of the olefin has been added (either with or without an inert gas employed to maintain the desired pressure), reaction is deemed complete in batchwise operations when the drop in pressure substantially ceases. When operating in a continuous, or semicontinuous fashion, a small amount of olefin under suitable pressure may continuously be added to the reaction mixture, or wax and olefin may both be continuously supplied to a suitable reaction zone, with the reaction mixture also being continuously withdrawn from said zone.

Once the reaction between the olefin and wax is complete, the resulting wax-olefin oil can then be separated from the other components of the reaction mixture by a practice of conventional refining techniques as more particularly described below in connection with the drawing. Briefly, however, the separation process normally involves a preliminary distillation to free the mixture of lighter ends (preferably those boiling below 250° F. at 1 mm. Hg) and thereby recover a light oil which is essentially comprised of polymerized olefin reactant. This is followed by a dewaxing step to remove unreacted waxes. Depending on the severity of the dewaxing treatment, oils are recovered having pour points of from below −65° F. to 10° F. The resulting dewaxed oil products have viscosities which are much the same as those of the molten waxy starting materials, and vary from about 33 to 80 or more SSU at 210° F. The viscosity index of the present oils normally is well in excess of 100 and preferably is 130 or more, except as lowered by the use of a blending oil.

The oil of this invention (apart from any blend thereof with mineral oil) is essentially comprised of the wax-olefin alkylation product resulting from the reaction of the wax with the olefin, this product normally comprising from about 60 to 95% by weight of the oil. The balance of the oil is made up essentially of polymerized olefin reactant. The relative amount of this component which is present depends upon the conditions which were employed in forming the oil, and particularly on whether or not said conditions favored polymerization of the olefins as well as on the severity of the distillation procedures practiced in recovering the oil from the crude reaction mixture. Thus, if desired, the wax-olefin oil of this invention can be obtained in a form substantially free of any polyolefin component by first carefully minimizing the amount of said polymer formed during the alkylation step, and by then subjecting the oil, either before or after the dewaxing step, to a distillation treatment which is rigorous enough to remove the more volatile olefin polymer. Inasmuch as distillation treatments of this character normally lead to serious losses of the wax-olefin alkylate, and since excellent results are obtained with oils containing even relatively large amounts of the polymer, the preferred practice is to obtain as final product an oil which contains from 70 to 90% of the wax-olefin alkylate and from 10 to 30% of the olefin polymer. The oils will also contain a small percentage (usually varying from a fraction of a percent up to about 4 or 5%) of various other materials such as unreacted waxes, partially cracked waxes, and the like. However, these materials make no particular contribution to the properties of the oil and may be regarded as impurities. They therefore have been disregarded in the foregoing statement of the preferred oil composition.

Reference is now made to the accompanying drawing which illustrates diagrammatically a process for carrying out one embodiment of the invention. According to this embodiment of the invention, olefin and wax are charged to a reactor, such as the coil reactor described in Example 1, either directly or into a mixing line or zone leading into the reactor. After reaction, the reaction products are introduced into a gas separation zone, wherein the light gases are separated from the heavier liquid fractions. Part or all of these light gases may then be bled off the system; or part or all of these gases may be recycled for use as olefins, preferably after treatment in an olefin concentration zone involving fractionation, adsorption or absorption, as is known in the art. The heavier liquid fraction from the gas separation zone is introduced into a distillation zone of one or more stills wherein a further separation light and heavy fractions is effected, the light fraction being recycled or bled off and the heavier fraction, dewaxed to give the wax-olefin oil of this invention. This wax, which may vary in amount from about 10 to 75% (in terms of the weight of wax charged) depending on the relative amount of olefin employed and the over-all severity of the reaction, is then available for further reaction with the olefin.

Referring to the drawing, the numeral **2** indicates a wax storage vessel or tank equipped with heating means, such as coil **3**, to render or maintain the wax fluid. The numeral **4** indicates storage vessel or tank for olefins, which may be introduced thereinto through valved line **5**, from an outside source, not shown. Fluid wax from storage tank **2** is introduced through line **7** into reactor **9**, while olefin material, for example, ethylene, is introduced thereinto through line **8**.

After reaction is complete, the reaction products are introduced through line **10** into gas separator **11**. Light fraction or gases are removed from the gas separator through line **12**. Part or all of these gases may be bled off through valved line **13** or part or all recycled to olefin storage **4** through line **14**. Overhead from gas separator **11** can be charged through line **15** to olefin concentrator **16**, wherein the olefins are concentrated, and then recycled through lines **17** and **14** to olefin storage, the saturated, or reject fraction being removed through line **18**. The heavier fractions from gas separator **11** are charged through line **19** to still **20** to effect a further separation of lighter and heavier fractions. The light fractions from still **20** are removed through line **21**, and part or all bled off through line **22** or part or all recycled through line **14** to olefin storage **4**. The heavier waxy oil fraction from still **20** is charged through line **23** to dewaxer **24** to obtain a low pour point oil through line **25**, and also wax, which may be recycled to wax storage through line **26**. The oil from line **25** may, if desired, be subjected to further distillation treatment to separate the oil into relatively light and heavy grades.

The oil of the present invention is well adapted to be

mixed with a hydrocarbon mineral oil to produce a variety of useful oil blends. Blends of this character which contain at least 50% of the wax-olefin oil described herein manifest relatively low deposit-forming characteristics when employed as the crankcase lubricant in internal combustion engines. Such blends are also well adapted to be used under sub-zero operating conditions for, by virtue of the inherently good viscosity index qualities of the present wax-olefin oils, it is possible to blend a low viscosity grade thereof with a higher viscosity grade of mineral oil and still obtain a blend having a low enough viscosity to permit ready starting of cold engines, yet which has good mileage characteristics as well. These mileage characteristics derive from the fact that even the lighter wax-olefin oils of this invention are relatively non-volatile, as are the heavier grades of mineral oil. Accordingly, a blend of a light wax-olefin oil with such a heavy mineral oil is relatively non-volatile at the elevated temperatures encountered in the engine once the engine is warmed up. The mineral oil employed in forming said blends can be derived from any refined solvent or acid-treated hydrocarbon oil, or mixtures thereof, as obtained from various crudes such as dewaxed paraffinic, naphthenic or wax-free mixed base crude oils, or from synthetic processes such as the Fischer-Tropsch process.

The present wax-olefin oils, whether employed alone, or in a mineral oil blend, are normally compounded with various additives in order to impart certain characteristics to the lubricant and adopt the same for use in internal combustion engines. Thus, to enhance engine cleanliness there is conventionally employed a detergent material, materials of the type including the metal phenates, sulfurized metal phenates, metal salts of alkyl phenol sulfides and polysulfides, metal sulfonates, metal phosphates and phosphonates, metal mercaptides, metal carboxylates, and the like, as well as various non-ashing detergents such as sorbitan monooleate, pentaerythritol monooleate and methacrylate/methacrylamide polymers. The total amount of detergent can be varied from about 0.1 per cent to 10 per cent and preferably constitutes from about 0.5 per cent to 5 per cent by weight of the final composition. In order to reduce oxidation and inhibit corrosion, corrosion and oxidation inhibitors are also normally added to the oil. Examples of suitable corrosion and oxidation inhibitors are organic sulfides and poly-sulfides, selenides and polyselenides, metal dithiocarbamates, salts and esters of organic thiophosphoric acids, and certain aromatic amines, such as phenyl alpha naphthylamine. These materials can be employed in total amounts of from about 0.1 per cent to 5 per cent by weight of the composition. As indicated above, when it is desired to improve the viscosity index of the composition, a viscosity index improving agent, such as a polymeric ester of methacrylic acid, can also be incorporated in the composition in an amount up to about 10 per cent and preferably between about 0.5 per cent and 5 per cent by weight. Other additives such as defoaming agents and metal deactivators can also be employed, as may extreme pressure agents and the like.

The following examples illustrate the present invention in various of its embodiments.

EXAMPLE 1

Ethylene was pumped from a storage tank into a mixing line where it was mixed with 125–130 AMP molten wax feed from a steam-heated feed tank by means of a pump. The mixture of ethylene and molten wax was charged to a reactor consisting of coiled ½ inch steel pipe mounted in a lead bath, the capacity of the reactor being 700 cc. The temperature of the reactor was maintained at about 660° F. by means of the lead bath, while the pressure in the reactor was held at 1900 p. s. i. g. The wax was fed to the reactor at a rate of 0.273 gm./cc. of reactor volume/hr., while the ethylene was fed at the rate of 0.148 gm./cc. of reactor volume/hr. The liquid product on being topped yielded 12.2 gms. of light oil boiling above 650° F., and the residue, on being solvent dewaxed at —20° F. yielded 36.3 gms. of heavy oil having a —0° F. pour point, these figures being based on 100 gms. of wax feed. This heavy oil had a bromine number of 12, a viscosity at 210 of 38.7 SSU and a viscosity index at 145. In a companion operation conducted under the same general conditions, but with the use of 2% chloroform catalyst (based on the weight of wax fed), the yield of heavy oil was increased to 76.4 gms./100 gms. of wax fed.

EXAMPLE 2

In this example, 4500 gms. of a 160–165 AMP paraffin wax derived from petroleum and having a viscosity of 47.5 SSU at 210° F. were charged into a steel pressure vessel and heated to 655° F. The vessel was then pressured to 2500 p. s. i. g. by the addition of 1050 gms. of ethylene and 40 gms. of chloroform. With the addition of the ethylene and catalyst, the resulting exothermic reaction caused the temperature in the vessel to rise to about 670° F., and the temperature was then maintained at approximately this level for the balance of the operation. After an initial reaction period of 69 minutes, it was observed that the pressure had fallen to 1380 p. s. i. g., whereupon the second increment of ethylene (540 gms.) and chloroform (30 gms.) was added, thus restoring the pressure to 2500 p. s. i. g. After another reaction period of 68 minutes, the third increment of ethylene (510 gms.) and chloroform (30 gms.) was added. This was followed by a reaction interval of 79 minutes and then by the addition of the final increment of ethylene (425 gms.) and chloroform (30 gms.). After the vessel was heated for a final period of 130 minutes, still at a temperature of approximately 670° F., the gas pressure was released from the vessel, there being recovered 326 liters of gas (at 72° F.) found to be made up of 85% ethylene. A portion (441 gms.) of the liquid reaction mixture (6892 gms.) remaining in the vessel was then taken and distilled under vacuum until a stillhead temperature of 266° F. at 1 mm. Hg was reached. In this process there was distilled off 110 gms. of a light oil which was found to consist essentially of polyethylene. The bottoms remaining from the foregoing distillation treatment were then solvent dewaxed in a two-stage dewaxing operation, the last stage of which involved chilling the mixture to —20° F. and filtering. The resulting product was found to have the following characteristics:

A. P. I. gravity	37.7°
Bromine number	7
Viscosity at 210° F	47.8 SSU
Pour point	—5° F.
Viscosity index	137

The foregoing oil had an average molecular weight of about 450 and was calculated to contain about 26% by weight of polyethylene. This oil was then again distilled in vacuo to remove the portion thereof (27.5% by volume) boiling below 415° F. at 0.3 mm. Hg. The remaining oil had the following properties:

A. P. I. gravity	37.2°
Bromine number	4
Viscosity at 210° F	54.2 SSU
Viscosity index	134
Pour point	0° F.
A. S. T. M. color	1.5 to 2

This final oil product had an average molecular weight of about 500 and was calculated to contain 17% by weight of polyethylene.

EXAMPLE 3

An oil prepared in the same fashion as described above in Example 2 was subjected to test as the crankcase lubricant in a Lauson one-cylinder engine and in an Oldsmobile Model 88 engine, the purpose of these tests being to determine the increase in octane requirement observed

as the initially clean engine was run using a commercial isooctane fuel.

The Lauson engine was operated continuously for 240 hrs. at full throttle (1200 R. P. M.) using a 15° spark advance, a jacket temperature of 210° F., a sump temperature of 150° F. and an air/fuel ratio of approximately 14:1 by weight. At the end of this period the octane requirement had increased by only 22 research numbers when the wax-olefin oil of this invention was used. In a companion test conducted under the same circumstances, but with a highly refined, wax-free base oil of SAE 30 grade having a viscosity index of 85 and derived from California Waxy crude, the octane increase was 43 research numbers.

The Oldsmobile engine was operated for a continuous period of 240 hours at 2000 R. P. M., with 35° spark advance, a load of 16 brake horsepower, a jacket temperature of 180° F., and a sump temperature of 165° F. Here the octane requirement increased was 5 research numbers with the wax-olefin oil and 14 research numbers with the mineral oil as defined in the foregoing paragraph.

EXAMPLE 4

In this example a micro-crystalline wax mixture obtained from petroleum oil and melting above 175° F. which had a viscosity of 80 SSU at 210° and an estimated viscosity index of 122 was employed. In carrying out the operation 600 gms. of the wax were charged to a pressure bomb and heated to 665° F. To the bomb was then charged 150 gms. of ethylene and 10 gms. of chloroform, the pressure in the bomb then being 1650 p. s. i. g. The bomb was then heated for a period of 74 minutes at a temperature of about 670° F., after which a further increment of 100 gms. of ethylene and 5 gms. of chloroform were added. The heating was then continued for a further period of 127 minutes, the pressure in the bomb being 1250 p. s. i. g. at the end of this second heating period. On releasing the gas from the bomb there was recovered 710 gms. of liquid product. 118 gms. of this product were then topped to remove the portion (5.3 gms.) boiling below 395° F. (pot temperature) at 1 mm. Hg. The remainder of the liquid product was then solvent dewaxed at —20° F., whereby there was recovered 55.3 gms. of a wax-olefin oil having a pour point of 0° F., a viscosity of 63.2 SSU at 210° F. and a viscosity index of 135.

EXAMPLE 5

About 400 gms. of AMP 125–130 wax (molecular weight about 375), 215 gms. of ethylene and 10 gms. of chloroform were charged to a bomb. The pressure in the bomb was then 1000 p. s. i. g. The bomb was heated to a temperature of about 640° F. over a period of 12 hours and was then held at this temperature for 5¾ hours, the pressure being 1600 p. s. i. g. as the bomb reached 194° F., 3290 p. s. i. g. at a bomb temperature of 507° F., and 1600 p. s. i. g. as the final temperature of 640° F. was reached. At the end of the 5¾ hour heating, the pressure in the bomb had dropped to 650 p. s. i. g. On releasing the gas pressure within the bomb, there was recovered 586 gms. of liquid reaction mixture which was then distilled to remove the portion boiling below 330° F. at 2.5 mm. Hg. The heavier oil recovered was then solvent dewaxed at —15° F., thereby yielding 401 gms. of oil having a pour point of 5° F., a viscosity of 41.5 SSU at 210° F., and a viscosity index of 143. When this oil was more severely dewaxed (at —50° F.), there was recovered 369 gms. of oil having a pour point of —35° F., a viscosity of 41.5 SSU at 210° F. and a viscosity index of 139.

EXAMPLE 6

The wax-olefin oil having the —35° F. pour point, whose preparation is described in the previous example, was blended with a neutral mineral oil which was a solvent refined, California paraffin base oil having a viscosity of 150 SSU at 100° F., a viscosity index of 87 and a pour point of —5° F., blends being prepared containing between 10% of the wax-olefin oil and 90% of the mineral oil to 90% of the wax-olefin oil and 10% of the mineral oil. These blends were miscible at all temperatures down to the pour point of the particular blend involved. For the sake of comparison, blends were made of the same mineral oil with a conventional synthetic oil of the polyglycol type, the particular polyglycol chosen being a methyl phenyl diether of polypropylene glycol having a molecular weight of about 1000. The blends so prepared were miscible only at relatively elevated temperatures; thus, a blend comprising 60% of mineral oil and 40% of the polyglycol was miscible only at temperatures above 72° F. When the mineral oil was blended with an equal amount of a synthetic oil comprising a methyl sec. butyl diether of polypropylene glycol having a molecular weight of about 500, it was found that the blend was compatible only at temperatures above 18° F.

In another series of tests the wax-olefin oil referred to above was blended with various of the additives which are customarily employed in lubricating oils. In one such test the oil was found to be compatible with a total of at least 100 millimoles of a calcium petroleum sulfonate and sulfurized calcium phenate per kg. of oil, the phenate normally being used in the proportion of approximately 2 moles for each mole of the sulfonate. On the other hand, it was found that amounts as small as 5 millimoles of said additives per kg. of oil would precipitate out at room temperature from a conventional polyglycol oil, here a monooctyl ether of polyglycol acetate having a molecular weight of about 500.

It was also observed that the additive-containing wax-olefin oils were not compatible with water and that even agitation of the compounded oil with water did not affect the composition. On the other hand, the polyglycol compositions were found to be readily compatible with water and the presence of as little as 0.2% by weight of water therein had the effect of causing the immediate decomposition, and precipitation from the mixture, of the phenate additive.

EXAMPLE 7

In this operation 100 parts of commercial eicosane, which contained 6 parts of oil having a 0° pour point, were reacted in a pressure vessel with 45 parts of ethylene for a period of one hour at an average temperature of about 670° F., the pressure at the beginning of the reaction being 2650 p. s. i. g. and at the end of the reaction, 1600 p. s. i. g. On distilling off the portion of the reaction mixture boiling below 250° F. at 1 mm. Hg and then solvent dewaxing the remaining liquid at —20° F., there was recovered 31.3 parts of a heavy oil having a pour point of 0° F., a vis. of 37 SSU at 210° F., and a viscosity index of about 130. When the foregoing run was repeated, but with the addition of 2 parts of chloroform as catalyst, the yield of heavy oil of 0° pour point was increased to 51.4 parts. In each of these reactions, there was recovered approximately 29 parts of unreacted ethylene.

The runs described in the preceding paragraph were then repeated, using 2-hour and 4-hour reaction periods, respectively. With the use of chloroform catalyst the amount of heavy oil recovered was 60 and 85.5 parts at 2 and 4 hours respectively, while in the uncatalyzed runs the increase in the yield of heavy oil was such as to yield 34.4 parts and 42.4 parts as reaction periods of 2 and 4 hours were employed.

Again repeating the foregoing runs with catalyst, but at 620° F., it was found that the 2- and 4-hour reaction periods resulted in the production of 41 and 53.6 parts, respectively, of heavy oil of 0° F. pour point.

EXAMPLE 8

This operation was conducted by employing the same reaction conditions as described in the first paragraph

of Example 7 above, except that here ethylene was replaced by an equivalent amount of propylene. When no catalyst was employed, with a 2-hour reaction period, the yield of 0° F. pour point oil was 18.7 parts per 100 parts of the eicosane starting material. On the other hand, by employing 2.3 parts of chloroform catalyst, the yield of heavy oil was increased to 30.5 parts. Extending the reaction period to 4 hours had the effect of increasing the yield of heavy oil to about 26 parts (in the absence of catalyst) and to about 45 parts with the employment of 2.4 parts of chloroform catalyst.

EXAMPLE 9

In this example eicosane was subjected to reaction first alone and then in the presence of ethane and chloroform. The first reaction involved heating 100 parts of eicosane, in a suitable pressure vessel, to 662° F. and maintaining the contents of the vessel at that temperature for 5 hours. On distilling the resulting product in vacuo to obtain a light oil fraction, and then solvent dewaxing the higher boiling materials at —20° F., there was obtained a total of but 7.2 parts of both light oil and the heavier 0° F. pour point material. Since the eicosane starting material (which was of commercial grade) contained 6 parts of 0° F. pour point oil, this is evidence that substantially no reaction occurred during the heating of the eicosane.

To determine whether the presence of a catalyst would have any effect on the reactivity of eicosane in the absence of any olefinic reactant, though under elevated pressure conditions, 300 parts of commercial eicosane were heated to 660° F. At this point the pressure vessel was charged with 134 parts of ethane and 6 parts of chloroform. The vessel, at an initial pressure of 2100 p. s. i. g., was now heated for 2 hours at 660° F. At the end of this time the pressure in the vessel was still 2100 p. s. i. g. The liquid product was then worked up by topping off a small amount of a light oil and by then solvent dewaxing the residue at —20° F. Here again, however, as in the operation described in the preceding paragraph, the total amount of light and heavy oils recovered did not appreciably exceed that contained in the eicosane starting material.

EXAMPLE 10

This operation was conducted to compare the efficacy of a number of different catalysts. The procedure employed with each catalyst was to react 300 parts of commercial eicosane with approximately 150 parts of ethylene at a temperature of about 670° F. for a period of 4 hours. The resulting liquid reaction mixtures were treated by topping to remove the lighter oil fraction boiling below about 250° F. at 1 mm. Hg and by then solvent dewaxing the residue at —20° F. to determine the amount of 0° F. pour point oil produced during the reaction. In the table below, which lists the catalyst employed, the amount of 0°F. pour point oil is expressed in terms of parts per 100 parts of the eicosane starting material employed.

Table I

Catalyst	Amt. of 0° F. Pour Point Oil Produced
None	42
$CHCl_3$ (6 parts)	86
CH_2Cl_2 (7 parts)	60
$CHCl_2F$ (11 parts)	65
HCl (7 parts)	47
$ZnCl_2$ (7 parts)	44
BF_3 (7 parts)	39

From the above data, it will be observed that the HCl, $ZnCl_2$ and BF_3 materials exerted substantially no catalytic, or even an anti-catalytic effect.

EXAMPLE 11

300 parts of wax (M.P.=125–130° F., M. W.=375), 300 parts of 2-butene and 6 parts of chloroform were charged to a bomb. The bomb was heated to about 670° F. over a period of 5 hours and held at this temperature for an additional period of 8 hours. A yield of 465 parts of liquid product was obtained which after distillation to remove light overhead left 443 parts of heavy oil boiling above 365° F. at 4 mm. of mercury pressure. This oil was dewaxed at —55° F. using methyl isobutyl ketone as a solvent yielding 88 parts of oil having the following properties:

Viscosity, centistokes:	
0° F.	662.5
100° F.	19.6
130° F.	11.34
210° F.	4.06
Viscosity index	122
Pour point, °F.	—20

EXAMPLE 12

814 parts Minas crude oil, 425 parts ethylene and 19 parts chloroform were charged to a bomb and heated at a temperature of about 650° F. for 10 hours.

A yield of 993.6 parts of liquid product was obtained after reaction. A comparison of the properties of this liquid with those of the original crude oil are as follows:

Property	Original Crude	Treated Crude
Gravity, °API	35.8	37.2
Pour Point, ° F	+95	Below —60
Fraction boiling above 430° F. at 1 mm. Hg:		
Oil, percent	17.6	26.2
Wax, percent	20.2	3.8
Asphaltenes, percent	2.0	0.2
Resins, percent	8.4	5.9

These data show that the lubricating oil content was materially increased by the treatment with ethylene at the expense of the wax, asphaltenes and resins.

A comparison of the properties of the lubricating oil before and after treatment follows:

	Original Crude	Treated Crude
Viscosity at 100° F. SSU	1110	955.4
Viscosity at 210° F. SSU	82.1	86.0
Viscosity Index	68	95

EXAMPLE 13

In many cases it is advantageous to remove the unsaturation present in the wax-olefin oils of this invention. This can readily be accomplished by hydrogenating the oil in the manner now described.

About 800 parts of oil prepared as in Example 1 was subjected to a maximum hydrogen pressure of 2,300 pounds per square inch, gauge, and a temperature of 392° F. for a period of time of six hours in the presence of 68 parts of Raney nickel. Properties of the oil before and after hydrogenation were as follows:

Properties	Hydrogenated Oil	Unhydrogenated Oil
Gravity, ° API	38.3	38.1
Bromine Number	2	12
Pour Point, ° F	20	10
Viscosity, centistokes:		
210° F.	4.6	4.7
130° F.	12.8	13.1
100° F.	22.2	22.6
Viscosity Index	143	145
Induction Period, Hours [1]	3.3	2.2

[1] Both oils compounded with 0.1% phenyl-α-naphthylamine, and the induction period, a criterion of oxidative stability, determined in accordance with the procedure and apparatus described in Industrial and Engineering Chemistry, vol. 28, p. 26 (1936).

EXAMPLE 14

In this operation, 400 parts cetane and 200 parts 2-methyl-1-butene were charged to a bomb. The bomb was heated to a temperature of about 660° F. over a period of five hours, and then kept at this temperature for eight hours. After reaction, 578 parts of liquid product was recovered. This product was topped by distillation to a temperature of about 320° F. at a pressure of 3.8 mm. of mercury. The bottoms, weighing 78 parts, had the following properties:

Gravity, °API	38.9
Bromine number	17
Molecular weight	360
Viscosity, centistokes:	
100° F.	13.68
130° F.	8.27
210° F.	3.23
Viscosity index	115

EXAMPLE 15

To a bomb there were charged 554 parts of cetane, 425 parts of ethylene and 23 parts of chloroform. The bomb was heated to a temperature of about 650° F. over a period of 8 hours and then kept at a temperature of about 640° F. for 8 hours. After reaction, 910 parts of liquid reaction products were obtained. This mixture was distilled to a temperature of about 270° F. at 2.7 mm. of mercury pressure to remove unreacted cetane. A yield of 639 parts of product boiling above cetane was then isolated. This liquid was subjected to dewaxing at −50° F. using methyl isobutyl ketone as the solvent. The yield of dewaxed oil was 248 parts. The oil had a molecular weight of 305, and a pour point of −45° F.

While the oils of the present invention find particular utility as crankcase lubricants in automotive and other types of internal combustion engines, they are also useful as torque or power transmitting fluids and as lubricants for many specialized applications, including the lubrication of gas turbines, gears, and aircraft engines. The lubricating oils of this invention may also be used advantageously as base oils for grease compositions. That is, the oils herein may be thickened to the consistency of greases by incorporating therein such thickening agents as metal soaps (e. g., calcium stearate, lithium hydroxy stearate, etc.), polymers of ethylene (i. e., linear solid ethylene polymers), inorganic aerogels (e. g., silica, thoria, etc.), polymeric nitrogen-containing compounds (e. g., polyamides obtained from amines and dibasic acids), and the like.

The utility of the present oils for many of the above purposes, particularly those relating to the use of said oils as gas turbine lubricants or as aviation oils or greases, is largely attributable to the fact that the slope of the viscosity curve of these oils decreases, or takes a downward turn, at lower temperatures, notably those which are well below 0° F. Thus, an oil derived by reacting eicosane with ethylene and which has a viscosity of 2.85 centistokes at 210° F. and of 11 centistokes at 100° F. and would, by extrapolation, be calculated to have a viscosity of 10,000 centistokes at −65° F., actually proves to have a viscosity of but 7,600 centistokes at −65° F.

Unless otherwise indicated herein, the parts or percentages given are on a weight basis.

We claim:

1. In a process for converting a normally solid hydrocarbon wax to a lubricating oil, the steps comprising reacting said wax with an olefin of from 2 to 10 carbon atoms in the presence of a hydrocarbyl halide catalyst at a temperature between 400 and 700° F. and at a pressure between 100 and 15,000 p. s. i. g.; and separating from the resulting reaction mixture the constituents boiling below 250° F. at 1 mm. Hg as well as the unreacted wax; the residual oil obtained in this fashion being characterized by a viscosity index of at least 100 and by a pour point not greater than about 10° F.

2. A lubricating oil produced by the method of claim 1.

3. The process of claim 1, wherein the olefin reactant is ethylene and the catalyst is an alkyl halide.

4. The process of claim 1, wherein the wax reactant is a hydrocarbon of predominantly open-chain configuration which contains from about 15 to 100 carbon atoms in the molecule, the olefin reactant is ethylene, and the catalyst is an alkyl halide.

5. In a process for converting a normally solid hydrocarbon wax to a lubricating oil, the steps comprising bringing said wax into reactive engagement with ethylene in the presence of a chloroform catalyst at superatmospheric pressure and at a temperature between 600 and 700° F., said reactants being employed in the proportion of from 1 to 25 moles of ethylene per mole of wax; distilling the lighter ends from the resulting reaction mixture; and treating the remaining heavy residue to remove unreacted wax therefrom; the resulting liquid oil product being characterized by a viscosity index of at least 100 and by a pour point not greater than about 10° F.

6. The process of claim 5 wherein the wax reactant is a paraffinic hydrocarbon containing from about 20 to 40 carbon atoms in the molecule.

7. The process of claim 5 wherein the wax reactant is eicosane.

8. In a process for producing a lubricating oil, the steps comprising reacting at least one normally gaseous olefin with a mixture of paraffin waxes of petroleum origin in the presence of an alkyl halide catalyst, said reaction being conducted at a temperature between about 600 and about 700° F. and at a superatmospheric pressure, and said reactants being employed in the ratio of from about 1 to 25 moles of the olefin for each mole of wax; and then isolating from the reaction mixture so obtained a lubricating oil having a viscosity index of at least 100 and a pour point not greater than about 10° F.

9. A lubricating oil produced by the method of claim 8.

10. The process of claim 8 wherein the olefin reactant is comprised predominantly of ethylene.

11. The process of claim 10, wherein the catalyst is chloroform.

12. The process of claim 10, wherein the catalyst is methylene chloride.

13. In a method for lowering the pour point of a wax-bearing material selected from the group consisting of wax-bearing crude oils, distillation and lubricating oils, the steps comprising reacting said wax-bearing material with at least one olefin of from 2 to 10 carbon atoms in the presence of an alkyl halide catalyst, said reactants being employed in the ratio of from 1 to 25 moles of said olefin for each mole of wax present in the waxy starting material, and said reaction being conducted at a temperature between 400 and 700° F. and under superatmospheric pressure.

14. The product produced by the method of claim 13.

References Cited in the file of this patent

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