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CONVERSION OF WAX INTO OIL

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This invention relates to the production of an improved lubricating oil and a process for producing this oil. More particularly, the invention concerns a process wherein hydrocarbon waxes of petroleum or other origin are treated catalytically to produce a lubricating oil having superior performance characteristics.

It has been ascertained that hydrocarbon waxes have good lubricating qualities when in the molten condition. Such waxes have good lubricity, a high viscosity index, and good stability. On the other hand, waxes have 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. An example of one such use, in addition to that as a crankcase lubricant for automotive and other internal combustion engines, is in jet engines of the type employed in modern aircraft where the lubricant must satisfactorily lubricate highly loaded bearings and gears at temperatures ranging from −65° F. to 700° F. and above. Accordingly, an object of the invention is to provide a process 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, and viscosity index qualities of the wax, thereby producing a novel synthetic oil having superior performance characteristics.

Other desirable characteristics of synthetic oils, in addition to having excellent lubricating and viscosity characteristics, are that they be fully compatible with, and respond well to treatment by, the various additives such as antioxidants, detergents, corrosion inhibiting agents, blooming agents and the like which are conventionally incorporated in lubricating oils. It is also desirable that the synthetic oil be compatible in all proportions with natural mineral oils. Compatibility with natural oils not only permits 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 replenishment of the main body of synthetic oil with a conventional oil, if need be, without danger of forming an incompatible mixture. A further object of this invention, therefore, is to provide from waxy hydrocarbons a novel synthetic oil of satisfactory pour point properties which, in addition to good lubricating, viscosity, and viscosity index qualities, has a high degree of compatibility with mineral oils and the various oil additives, and which has a high degree of response to treatment with such additives.

Another desirable property of a lubricant concerns the amount of deposit which the oil leaves upon use, particularly when burned in an engine, it being desirable that oils employed as automotive crankcase lubricants, or as lubricants for use in aircraft engines, leave as small a residue as possible. Combustion chamber deposits, whether attributable to the oil or to the fuel, have the effect of increasing the octane requirement of the engine,

and 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 engine is clean. Accordingly, an important object of the invention is 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 or in a gas turbine.

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

We have now discovered that the foregoing objects can be attained by a process which involves heating a suitable hydrocarbon wax, or mixture of said waxes, at temperatures between 600 and 800° F. in the presence of a catalyst made up of at least one reduced metal compound selected from the group consisting of cobalt oxide, nickel oxide and molybdenum oxide, said compounds being deposited on a support comprising activated alumina, which catalyst also contains at least one additive selected from the group consisting of vanadium oxide and tungsten oxide. It has been found that the introduction of such additives greatly increases the activity of the catalyst and makes it possible to obtain higher yields of the more desirable, heavier oil fractions than would otherwise be the case.

As indicated above, the catalyst employed in a practice of the present invention is one which incorporates a support of activated alumina. Such materials are well known in the art and their preparation need not be described here in particular detail, it being noted, however, that insofar as the present invention is concerned, the alumina employed should be one which is substantially free of alkali metal salts or oxides, though it may contain a small percentage of silica. Thus, the alkali metal content of the support should be kept below about 0.2% and preferably below 0.05% by weight. In general, satisfactory activated alumina catalyst supports have surface areas in excess of 20 m.^{2}/g. and can be prepared by methods such as those described in U. S. Patents Nos. 1,868,869 and 2,015,593, for example.

The cobalt, nickel and/or molybdenum oxides, along with the vanadium oxide and/or tungsten oxide additives, can be deposited on the activated alumina support in any one of a variety of ways, e. g., by impregnation or coprecipitation, the preparation being such, however, that the final catalyst will contain from about 0.1 to 20% each, in terms of the metal component thereof, of the cobalt, nickel and/or molybdenum oxides, and from about 0.1 to 10% each, in terms of the metal content thereof, of the said vanadium and/or tungsten oxides, preferred ranges being from about 0.5 to 5% by weight of metal for cobalt and vanadium and from about 1 to 10% for molybdenum, nickel and tungsten. Thus, a convenient method comprises impregnating activated alumina, in the form of granules or pellets of the desired size, with a solution of the desired metal compounds and then drying the product at the desired temperature, followed by a calcining step. In accordance with this procedure, alumina is heated under a reduced pressure to a temperature of about 550° F. to remove air from the pores thereof, followed by cooling the material and adding the impregnating solution under reduced pressure. If desired, impregnation of the activated alumina may be accomplished by covering it with the impregnating solution and alternately boiling and cooling, or the mixture may simply be allowed to stand for a sufficient period of time. The concentration of the impregnating solution used in each particular case will depend upon the solubility of the particular metal compound at the temperature of the impregnation and upon the desired concentration of the metal compound in the finished catalyst. If desired, a sequence of impregnation steps can be employed, with the catalyst being dried between each, in order to arrive at the final catalyst composition. The normal procedure in this or the single impregnation method is to employ only that amount of impregnating solution which can be fully taken up by the catalyst. Whatever the method of preparation, the catalyst is calcined and reduced in an atmosphere of hydrogen before being used.

In preparing the catalyst by the above alumina-impregnation method, representative molybdenum, cobalt and/or metal-containing solutions which can be employed are those of cobalt nitrate, ammonium molybdate, cobalt ammono-molybdate and nickel nitrate, as well as solutions containing two or more of these or other suitable salts. As regards the vanadium and/or tungsten components of the catalyst, suitable impregnating agents are a solution of tungstic acid or tungsten dioxydichloride in ammonium hydroxide or a tungsten acid-oxalic acid complex, or an aqueous solution of vanadium tribromide, vanadium trifluoride trihydride, vanadium tetrafluoride, vanadium pentafluoride, vanadium trioxide, vanadium oxydibromide, vanadium oxytribromide or variadyl sulfate. For a detailed description of the method by which representative catalysts suitable for employment in the present invention can be prepared, reference is made to Examples I and II hereof as given below.

An alternative method of preparing the catalyst is to coprecipitate aluminum hydroxide along with one or more of the other metal-containing compounds to be employed in the catalyst. On thereafter heating the resulting precipitate so as to convert the same to alumina and one or more other metal oxides, the product may thereafter be subjected to impregnation, if necessary, to provide the desired catalyst composition. Thus, a catalyst containing alumina and molybdenum oxide can be prepared by adding a suitable aluminum salt such as aluminum chloride, aluminum nitrate or aluminum acetate to a solution of ammonium molybdate in ammonia hydroxide with the precipitate so formed being water washed to remove water-soluble impurities and thereafter dried, ground and calcined. The resulting product may then be impregnated with a suitable solution of a vanadium or tungsten material and thereafter be again dried and calcined so as to provide a final catalyst composition containing the desired amount of vanadium oxide and/or tungsten oxide.

Whatever the catalyst be produced, it is necessary that the same be reduced by treatment with hydrogen prior to use. This reduction treatment is effected by heating the catalyst composition in the presence of hydrogen at atmospheric pressures at temperatures of from about 800 to 1100° F. for an appreciable period of time, usually on the order of from about 2 to 8 or more hours.

The waxy compound, or mixture of such compounds, to be converted to a low pour point oil in accordance with a practice of the present invention can be any hydrocarbon of predominantly open-chain configuration which contains from about 18 to 100 carbon atoms in the molecule. Included are various members of the paraffin series of hydrocarbons such as octadecane, eicosane, 2,19-dimethyleicosane, pentacosane, octacosane, triacontane, tritetracontane, heptacontane, and the like, as well as hydrocarbon compounds containing a long hydrocarbon chain such as tetradecylcyclohexane, octadecylbenzene, 2-octadecyldecalin, and hexadecylcyclopentane. Also included are various crystalline and microcrystalline paraffin waxes, including slack and petrolatum waxes and wax mixtures, ceresin, ozocerite and polyethylene waxes, as well as those derived from the Fischer-Tropsch synthesis or by the destructive or nondestructive hydrogenation of coal, shale oil or the like. These waxes 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 treated 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 microcrystalline waxes 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.

In carrying out the process of the invention the wax is maintained in liquid condition as obtained either by melting the wax or by employing a solution thereof in a solvent, e. g., 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 handle 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 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.

Whatever the nature of the waxy starting material, the liquid feed is passed through the catalyst in a suitable reaction zone at temperatures between 600 and 800° F., preferably 675 to 740° F., and at liquid hourly space velocities (L. H. S. V.) ranging from about 0.01 to about 4, and preferably 0.1 to 2. Elevated pressures have been found to exert a beneficial effect on the reaction though atmospheric pressures can be employed if desired. In general, it has been found that pressures above about 100 p. s. i. g. are preferred, the desired pressure being maintained in the reaction zone either hydrostatically, as by compression of the molten wax, or by means of an inert gas such as nitrogen. If desired, hydrogen gas may also be supplied along with the feed in amounts varying from about 0.1 to 10 moles per mole of wax. However, while the hydrogen has the effect of somewhat suppressing undesirable cracking reaction of the wax, the hydrogen also has the disadvantage of accelerating the rate at which the catalyst declines in activity with use. Accordingly, it is preferred that no hydrogen be employed as a component of the feed stream or be otherwise introduced into the reaction chamber from an external source.

As will occur to those skilled in the art, the reaction can be carried out by a practice of any one of the conventional methods now employed in catalyst reactions. Thus, there may be employed a fixed catalyst bed system in which the catalyst is disposed in a reaction zone, with the wax then being passed through the catalyst in any desired direction. Other processes which can be utilized are moving bed type systems wherein catalyst and wax are contacted countercurrently or concurrently, and the fluidized bed systems in which wax and catalyst are maintained in a turbulent state. Whatever the method employed, it is found that the catalyst becomes deactivated with use and can be regenerated in whole or in part by processes wherein the carbonaceous deposits formed on the catalyst during the reaction are removed by burning with a free oxygen-containing gas at temperatures of about 1000 to 1100° F., followed by a reduction treatment wherein the catalyst is heated in hydrogen for one or more hours at temperatures of from 800 to 1100° F.

The oil which is obtained as a result of the foregoing practice can be separated from the other components of the reaction mixture by a practice of conventional refining techniques. Briefly, the separation process normally involves a preliminary distillation to free the mixture of small amounts of lighter ends (usually those boiling below 650° F.), followed by a dewaxing step to produce an oil of 0° F. pour point or below, though the dewaxing step can be practiced at any other stage in the working-up operation. Depending on the severity of the dewaxing treatment, oils are recovered having pour points as low as −65° F. and lower. 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 oils prepared in accordance with the invention is normally well in excess of 100 and usually is of the order of 130 or more. If desired, the yield of low pour point oils can be increased by recycling the unreacted wax and/or the partially isomerized wax back to the reaction zone.

The process of the present invention is illustrated in various of its embodiments by Examples I to III given below. In each of these operations, a liquefied 160/165 AMP wax of petrolume origin having a naphthene content of about 20% and an average molecular weight of about 452, was passed through the catalyst at a space rate of 2 volumes per volume of catalyst per hour, and at a temperature 725° F. and pressure of 900±10 p. s. i. g. No added hydrogen was introduced with the feed stream. The product stream was separated into, first, a gas fraction, second, a light oil fraction obtained by distilling overhead from the reaction mixture the portion having an end point of approximately 650° F. at atmospheric pressure (385° F. at 10 mm. Hg), third, a heavy oil fraction (initial boiling point 650° F.) representing the remainder of the reaction mixture after dewaxing to 0° F. pour point, and, lastly, the wax removed to obtain an oil of 0° F. pour point which wax is considered as representing unconverted feed. The unmodified, or "control" catalyst, which was used as a basis for comparison with the other catalysts described in the examples was prepared by impregnating 2550 grams of pure activated alumina with a solution containing 196 grams of

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$$

220 ml. of concentrated (28%) NH_4OH, and 220 ml. of water, following which the material was dried for 16 hours at 170° F. and calcined for 1 hour at 1100° F.; 2140 grams of the resulting calcined product were then impregnated with a solution containing 227 grams of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 250 ml. concentrated NH_4OH, and 950 ml. of water, after which the material was again dried at 170° F. and calcined for 1 hour at 1100° F.; lastly, the product was reduced in a stream of hydrogen gas for 3 hours at 1000° F. This product contained an amount of molybdenum oxide, equivalent to 9% by weight of molybdenum. With this "control" catalyst, there is obtained 2.0% gas, 6.6% light oil, 49.4% heavy oil (650° F. initial, 0° F. pour point) and 42.0% unconverted wax.

Example I

The catalyst employed in this operation was made up of molybdenum oxide (9% Mo) and tungsten oxide (3% W) deposited on activated alumina. It was prepared by impregnating 170 parts by wt. of the "control" catalyst described above with 7.2 parts of H_2WO_4 in 35 parts concentrated (28%) NH_4OH and 60 parts of water, the impregnated material then being dried at 170° F. and calcined at 1100° F. for 1 hour and reduced in a stream of hydrogen gas for 2 hours at 1100° F. On now reacting the liquefied 160/165 AMP wax with this catalyst and fractionating the resulting reaction product in the same fashion as described in the preceding paragraph, it was found that the percentage of unreacted wax had

been reduced from 42% (in the case of the "control" catalyst) to 21.4%, there having been produced 3.1% gas, 18.9% light oil and 56.6% heavy oil (650° F. initial and 0° F. pour point).

Example II

In this operation, the catalyst described in Example I above, after being used for a number of hours, was regenerated by burning in air, following which it was reduced in a stream of hydrogen gas for 3 hours at 1000° F. In this case an analysis of the reaction product obtained by reacting the liquefied 160%-65 AMP wax in the same fashion as recited above in connection with the "control" catalyst disclosed the presence of 1.7% gas, 8.3% light oil and 66.4% heavy oil, the unconverted wax amounting to but 23.6% of the product.

Example III

The catalyst employed in this operation was made up of molybdenum oxide (9% Mo) and vanadium oxide (3% V) deposited on activated alumina. It was prepared by impregnating 170 parts of the "control" catalyst described above with 12.3 parts of NH_4VO_3 dissolved in 190 parts of hot water, the impregnation having been effected in 2 steps with 1 hour's calcining at 1100° F. intervening. The resulting catalyst was then dried at 170° F., calcined at 1100° F. for 1 hour and then reduced in a stream of hydrogen gas for 2 hours at 1050° F. When liquefied 160/165 AMP wax was reacted under the same reaction conditions as described in the preceding examples, it was found that the product contained 2.5% gas, 20.7% light oil, 55% heavy oil and but 21.8% unreacted wax.

Various percentages employed herein and in the appended claims are on a weight basis.

We claim:

1. The process of producing oil from a hydrocarbon wax, which comprises passing said hydrocarbon wax in the liquid phase and at a temperature between about 600 and 800° F., through a catalyst comprising activated alumina on which is deposited from 0.1 to 10% by weight, in terms of the metal component thereof, of at least one compound selected from the group consisting of the oxides of vanadium and tungsten, together with at least one metal oxide selected from the group consisting of molybdenum oxide, cobalt oxide and nickel oxide.

2. The process of producing oil from a hydrocarbon wax, which comprises passing said wax, at a liquid hourly space velocity of from about 0.01 to 4, at a pressure of at least 100 p. s. i. g., in the liquid phase and at a temperature between 600 and 800° F., through a catalyst comprising activated alumina on which is deposited from 0.1 to 10% by weight, in terms of the metal component thereof, of at least one compound selected from the group consisting of the oxides of vanadium and tungsten, together with from 0.1 to 20% by weight, in terms of the metal component thereof, of at least one metal oxide selected from the group consisting of molybdenum oxide, cobalt oxide and nickel oxide.

3. The process of producing oil from a hydrocarbon wax, which comprises passing wax at a liquid hourly space velocity of from about 0.01 to 4, at a pressure of at least 100 p. s. i. g., in the liquid phase and at a temperature between 600 and 800° F. through a catalyst comprising activated alumina on which is deposited from 0.1 to 10% by weight each of molybdenum oxide and vanadium oxide, in terms of the metal components of said oxides, and recovering the desired oil fraction from the resulting reaction mixture.

4. The process of producing oil from a hydrocarbon wax, which comprises passing wax at a liquid hourly space velocity of from about 0.01 to 4, at a pressure of at least 100 p. s. i. g., in the liquid phase and at a temperature between 600 and 800° F. through a catalyst comprising activated alumina on which is deposited from 0.1 to 10% by

weight each of molybdenum oxide and tungsten oxide, in terms of the metal components of said oxides, and recovering the desired oil fraction from the resulting reaction mixture.

5. In a process for producing oil from a hydrocarbon wax, the steps comprising passing said wax at a liquid hourly space velocity of from about 0.01 to 4, a pressure of at least 100 p. s. i. g., in the liquid phase and at a temperature between 600 and 800° F., through a catalyst comprising activated alumina on which is deposited from 0.1 to 10% by weight, in terms of the metal component thereof, of at least one compound selected from the group consisting of the oxides of vanadium and tungsten, together with from 0.1 to 20% by weight, in terms of the metal component thereof, of at least one metal oxide selected from the group consisting of molybdenum oxide, cobalt oxide and nickel oxide, fractionating the resulting reaction mixture to recover a heavy oil fraction boiling above 650° F., and dewaxing said heavy oil fraction to obtain a lubricating oil of the desired pour point.

6. The process of claim 5 wherein the wax comprises a mixture of paraffin waxes of petroleum origin.

7. The process of claim 5 wherein the wax comprises a mixture of napthene-containing hydrocarbon waxes of petroleum origin.

8. The process of claim 7 wherein the heavy oil fraction is subjected to a dearomatization step to produce an oil having reduced deposit forming characteristics at high temperatures.

9. The process of claim 8 wherein the dearomatization step is one of hydrogenation.

10. In a method for lowering the pour point of a wax-containing material selected from the group consisting of wax-bearing crude oils, distillates and lubricating oils, the step comprising passing said wax-bearing material at a liquid hourly space velocity of from about 0.01 to 4, a pressure of at least 100 p. s. i. g., in the liquid phase and a temperature between 600 and 800° F., through a catalyst comprising activated alumina on which is deposited from 0.1 to 10% by weight, in terms of the metal component thereof, of at least one compound selected from the group consisting of the oxides of vanadium and tungsten, together with from 0.1 to 20% by weight, in terms of the metal component thereof, of at least one metal oxide selected from the group consisting of molybdenum oxide, cobalt oxide and nickel oxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,399,927	Howes et al.	May 7, 1946
2,426,929	Greensfelder	Sept. 2, 1947
2,608,534	Fleck	Aug. 26, 1952
2,668,790	Good et al.	Feb. 9, 1954
2,668,866	Good et al.	Feb. 9, 1954
2,787,582	Watkins et al.	Apr. 2, 1957
2,799,661	De Rosset	July 16, 1957