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LUBRICANTS

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This invention relates to a method of preparing multipurpose lubricant additives by irradiation, and to lubricating compositions containing these additives.

One of the desirable properties of a lubricating oil is a high viscosity index. A high viscosity index means that the oil is subject to less change in viscosity with changes of temperatures as compared to oils having a lower viscosity index. Another desirable property of a lubricant is resistance to shearing action or shear stability. It is further desired that lubricating oils have a low pour point so that they will function effectively at relatively low temperatures. These requirements are particularly important in the lubrication of internal combustion engines, especially today's high compression automotive engines. There is a continuing need for improved lubricants having satisfactory properties.

It has now been unexpectedly found that normally solid paraffin wax constitutents, usually removed from lubricating oils during their preparation, can be converted to obtain potent lubricating oil additives by high intensity ionizing radiation comprising, preferably, neutrons and gamma rays. The additives prepared by the method of this invention substantially and favorably affect viscosity index, pour point, shear stability, and other properties when used in minor amounts in lubricating oil compositions.

In brief compass, this invention proposes a process for preparing a lubricating additive. This process comprises irradiating a paraffin wax fraction containing at least 80 wt. percent of paraffin hydrocarbons having from 21 to 32 carbon atoms, with high intensity ionizing radiation comprising neutrons. Preferably, the intensity of radiation of both gamma rays and neutrons is above 10^5 roentgens/hr., and the total dosage received by the fraction is at least 10^4 ergs/gm./sec. A surprising feature of this invention is that very high conversions, usually over 90%, are obtained. In many cases the conversion is substantially complete. The conversion is preferably carried out in the presence of a porous solid hydrocarbon conversion catalyst.

The product obtained by this treatment is a relatively hard rubbery material at room temperatures. This rubbery material is soluble in oil, whereas some irradiated solid products, such as that obtained from the irradiation of cetane, are only slightly soluble, if at all.

The material converted by the present invention is essentially paraffin waxes having the formula

$$C_nH_{2n+2}$$

where n is a positive integer having a value from about 21 to 32, preferably 24 to 29. The paraffin waxes used in the present invention have a preferred melting point in the range of 120 to 150° F., and a boiling point in the range of 735° to 840° F. at atmospheric pressure. While some dilution of the reactants is permissible, it is preferred that the reactant fraction contain at least 80 wt. percent of the above identified hydrocarbons, including mixtures thereof.

These normally solid paraffin waxes or wax fractions can be obtained by any convenient method, such as by distillation, extraction, absorption, adsorption, filtering and the like. They are normally obtained by solvent (propane or ketone) dewaxing processes. They can be obtained from a variety of crude oils such as, for example, East Texas, Panhandle, Louisiana, San Joaquin, mid-Pennsylvania, and the like. The waxes used, preferably, have the following composition: greater than 70% straight chain paraffins, less than 20% iso- or branch chain paraffins, and less than 10 wt. percent of naphthene or saturated cycle rings.

It is an important feature of this invention to exclude paraffins having under 20 carbon atoms, because these lower molecular weight hydrocarbons do not give equivalent results. For example, the product obtained from them is quite amenable to thermal degradation. Also, the product obtained from C_{21}–C_{32} waxes is much more oil soluble than the product obtained from irradiation of hydrocarbons having less than 20 carbon atoms.

The irradiation used in the present invention can be obtained from particle accelerators, nuclear waste products such as spent fuel elements, or products especially made radioactive such as cobalt 60. When using radioactive materials, it is preferred that the average gamma ray flux in the reaction zone be better than about 10^4 roentgens/hr., and the conditions be such that the paraffin wax receive at least 10^4 ergs/gm./sec. of gamma ray irradiation. The material can be continuously exposed to the radiation source simply by flowing it in pipes past or through the radioactive material, or can be exposed in batchwise manner.

It is much preferred, however, to use a nuclear reactor as the radiation source. In this embodiment of the invention, it is preferred to have the average gamma ray flux in the reaction zone above 10^5 roentgens/hr., and the average neutron flux above 10^{10} neutrons/cm.^{2}/sec. The total dosage received by the paraffin wax is above about 10^4 ergs/gm./sec.

When using a nuclear reactor, the hydrocarbon oil can simply be flowed through pipes disposed in, around, or near the fissionable material. Conventional moderators such as carbon and water can be used. In some cases, the hydrocarbon reactant can serve as a moderator.

The irradiation is preferably carried out in liquid phase and for that reason, the pressure is preferably sufficient to maintain substantially liquid phase conditions, although it may range from 10 to 1000 p.s.i. The temperature is preferably below thermal cracking temperatures, i.e., below 700° F., although it can range from 0 to 900° F. The time of treatment, which is dependent upon the radiation intensity, is sufficient to obtain the above dosages and will usually lie in the range of 10 to 10^4 minutes.

Preferably, the conversion of the oil is carried out to an extent sufficient to obtain at least 75 wt. percent of the product as an isomerized lubricant or additive.

Inorganic solids such as absorbents and/or catalysts can be used during irradiation. Thus, materials such as kieselguhr, carbon or coke, cracking catalyst, hydrogenation catalyst and the like can be used. This solid material can exist as fixed or fluidized beds in the reaction zone, or a suspensoid system can be used. The solids can be regenerated if necessary, either continuously or periodically, either in or external of the reaction zone by such means as chemical reworking and burning.

Materials that given off secondary radiation upon neutron capture or photon incidence such as boron 10, lithium 6, cadmium 113, beryllium 9 can also be used if desired. They can be used as pure or concentrated isotopes, or as natural elements containing these isotopes. They can be carried on solids such as those above identified, exist as discrete solids in themselves, or can be used in solutions, e.g., tri-n-dodecyl borate can be used.

After irradiation, the reactants can be further treated as desired as by filtration, distillation, absorption, adsorption, extraction, crystallization and ion exchange,

etc. Portions of the separated product can be recycled if desired.

It is preferred to separate as the improved additive of this invention, a material from the reactants that has a boiling point above about 950° F. at atmospheric pressure, and a melting point within the range of 400 to 700° F. The additive obtained should be chemically and thermally stable and should be an oil soluble, rubbery product.

In accordance with the present invention, an improved lubricating oil is obtained by combining this additive obtained by the irradiation with a lubricating oil or grease base stock. Generally, the lubricant compositions comprise a major proportion, i.e., greater than 96 wt. percent of a lubricating oil, and a minor but effective proportion, i.e., preferably less than about 4 wt. percent of the above additive, although greater amounts can be used. Conventional lubricating oils can be used such as mineral, animal, vegetable and/or synthetic (e.g., di-2-ethyl-hexylsebacate) lubricating oils.

Preferably, the lubricating oil base stocks used have a boiling point in the range of 700 to 1200° F. and an S.S.U. viscosity at 210° F. in the range of 40 to 300. With such materials, usually 0.1 to 4 wt. percent of the additive of this invention will be used in the composition.

It will be understood that the present lubricant compositions may include conventional lubricant additives. More particularly, the lubricating oil compositions may contain detergents (e.g., barium tertiary octyl phenol sulfide), oxidation inhibitors (e.g., phenyl alpha naphthylamine), corrosion inhibitors (e.g., zinc dihexyl dithiophosphate), viscosity index improves (e.g., polyisobutylene), rust inhibitors, dyes, anti-foaming agents, etc., in minor proportions. The lubricating grease compositions may contain conventional grease thickeners such as fatty acid soaps (e.g., calcium stearate), soap-salt complex thickeners (e.g., calcium acetate-calcium stearate), inorganic thickeners such as silica, carbon, etc., polyethylene, polybutene, oxidation inhibitors, corrosion inhibitors and the like in minor proportions.

Preferably, the lubricating composition containing the additive of this invention has a viscosity in the range of 40 to 300 S.S.U. at 210° F., a boiling point in the range of 700 to 1200° F., a viscosity index above 100, and a pour point below 10° F. In some applications, however, this additive can be used effectively in low (50–70) viscosity index oils.

EXAMPLE 1

The wax was a paraffin 700/900° F. distillate from San Joaquin crude. It was de-oiled to 3% oil and further reduced in oil content to 0.3% oil by sweating processes. This wax melts at 125° F. and contains 99% n-paraffins and 1% non-normal paraffins.

The above feed stock was converted in an atomic pile in the presence of two different types of hydrocarbon conversion catalysts, namely, a silica-alumina cracking catalyst and a platinum on alumina hydroforming catalyst.

The platinum on alumina catalyst was a commercially available alcoholate alumina catalyst containing 0.6 wt. percent platinum and 0.6 wt. percent chlorine, known as Davison type 1000. The catalyst was in the form of 3/16-inch by 1/8-inch cylinders having a surface area of 300 $m.^2/gr.$, and a pore size of 50 to 80 A.

The silica-alumina catalyst was made by precipitating alumina from an aluminum sulfate solution on previouly precipitated silica by the addition of ammonia. The precipitate was washed, dried and calcined for several hours at about 1200° F. The catalyst contained 13% alumina and was formed in 3/16 by 3/16-inch diameter pills. The final catalyst had a surface area of about 500 $m.^2/gr.$

The air-cooled, natural uranium, graphite moderated research reactor of the Brookhaven National Laboratories was used to irradiate the samples. The pile was operating at a total power of about 24 megawatts at the time of these experiments. The thermal neutron flux in the reaction zone was $2.5\times10^{12}/cm.^2/sec.$ The fast neutron flux (greater than 1 mev.) was $0.5\times10^{12}/cm.^2/sec.$, and the gamma ray flux was 1.6×10^6 roentgens/hr.

The core of the reactor was approximately a 20 ft. x 20 ft. lattice of graphite with horizontal one-inch diameter aluminum clad uranium rods spaced evenly through the reactor, and extending from the north to south faces of the core. The core was completely surrounded by 5 ft. of concrete shielding. The sample holes used for irradiation were horizontal 4-inch square holes extending through the 5 ft. concrete shield, and into the carbon core for a distance of 10 ft. Normal operating temperatures in the experimental hole were about 250–400° F.

Five hundred cc. of catalyst and 500 cc. of the paraffin wax were irradiated in a vented 3-inch diameter aluminum container mounted on a horizontal aluminum sled. Vents of aluminum tubing extended from the vapor space in the containers to a sample receiving system on the outside of the shielding. Gases and condensible liquids from the vents were metered and collected. The samples were inserted in the pile during the scheduled shutdowns, irradiated for a period of 10 days, and were then withdrawn from the pile during the following shutdown.

It was found under these conditions that more than 95 wt. percent based on paraffin wax feed was converted to a rubbery material resembling a brittle eraser. This material was oil soluble and conversion was essentially complete. The rubbery polymer began to liquefy in a nitrogen atmosphere at 550° F. and was completely liquid at 650° F. with no loss of weight under these conditions.

EXAMPLE 2

The above rubbery material was added to a lubricating oil that already contained a pour depressant. The lubricating oil had the following inspections:

Pour point	−20° F.
Viscosity index	114.
Viscosity	45.88 S.S.U. at 210.
Boiling range	700/1000° F.

Three wt. percent of the rubbery polymer was added to the oil, and the following inspections were obtained:

Table I

Catalyst	Viscosity				V.I.	Pour Point, ° F.
	S.S.U. at 210	S.S.U. at 100	Kinematic at 210	Kinematic at 100		
Base Oil	45.88	175.0	6.00	37.54	114	−20
Pt.-Alumina	46.92	184.0	6.32	39.46	120	−25
Silica-Alumina	47.56	189.0	6.50	40.58	122	−25

These data clearly show that the rubbery polymer made from wax has considerable V.I. improving properties and, at the same time, pour depressant properties even in a base stock already containing pour depressant.

EXAMPLE 3

The rubbery material obtained by the irradiation of the paraffin wax was added to a lubricating oil base stock. The base stock had a viscosity of 47.9 S.S.U. at 210° F. The following inspections were obtained:

Table II

Catalyst	Rubber (Wt. percent)	V.I.	Pour Point, ° F., of Solution
Base Oil		113	+15
Silica-Alumina	3	118	−10
Silica-Alumina	5	120	−10
Pt.-Alumina	3	116	0

These data clearly show that the rubbery polymer has considerable pour depressant and V.I. additive properties at the same time and is, therefore, a general additive.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A lubricating oil composition comprising a major proportion of a lubricating oil base stock and in the range of about 0.1 to about 4 wt. percent of an additive prepared by irradiating a paraffin wax fraction containing at least 80 wt. percent of paraffin hydrocarbons having from 21 to 32 carbon atoms with high intensity ionizing radiation to an extent that said fraction receives a dosage above at least 10^4 ergs/gm./sec. for a time sufficient to convert at least 75 weight percent of said fraction to an oil soluble rubbery additive material, said lubricating oil composition having a viscosity in the range of 40 to 300 S.S.U. at 210° F., a boiling point in the range of 700 to 1200° F., a viscosity index above 100, and a pour point below 10° F.

2. The composition of claim 1 wherein said paraffin hydrocarbons have from 24 to 29 carbon atoms.

3. A lubricating oil composition according to claim 1 wherein said rubbery additive material has a boiling point above 900° F. and a melting point in the range of about 400° to 700° F.

4. A lubricating oil composition according to claim 1 wherein said wax fraction is irradiated in the presence of a porous solid hydrocarbon conversion catalyst.

5. A lubricating oil composition comprising a major proportion of a lubricating oil base stock and in the range of about 0.1 to about 4 weight percent of an additive prepared by irradiating a paraffin wax fraction containing at least 80 weight percent of paraffin hydrocarbons having from 21 to 32 carbon atoms with high intensity ionizing radiation to an extent that said fraction receives a dosage above at least 10^4 ergs/gm./sec. for a time sufficient to convert at least 75 weight percent of said fraction to an oil soluble rubbery additive material.

6. A lubricating oil composition comprising about 97 weight percent of a lubricating oil base stock and about 3 weight percent of a rubbery additive material prepared by irradiating 500 cc. of a de-oiled paraffin 700/900° F. distillate in the presence of 500 cc. of a platinum-alumina hydrocarbon conversion catalyst with high intensity ionizing radiation to an extent that said paraffin distillate receives a dosage above at least 10^4 ergs/gm./sec. for a time sufficient to convert at least 75 weight percent of said distillate to an oil soluble rubbery additive material.

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