

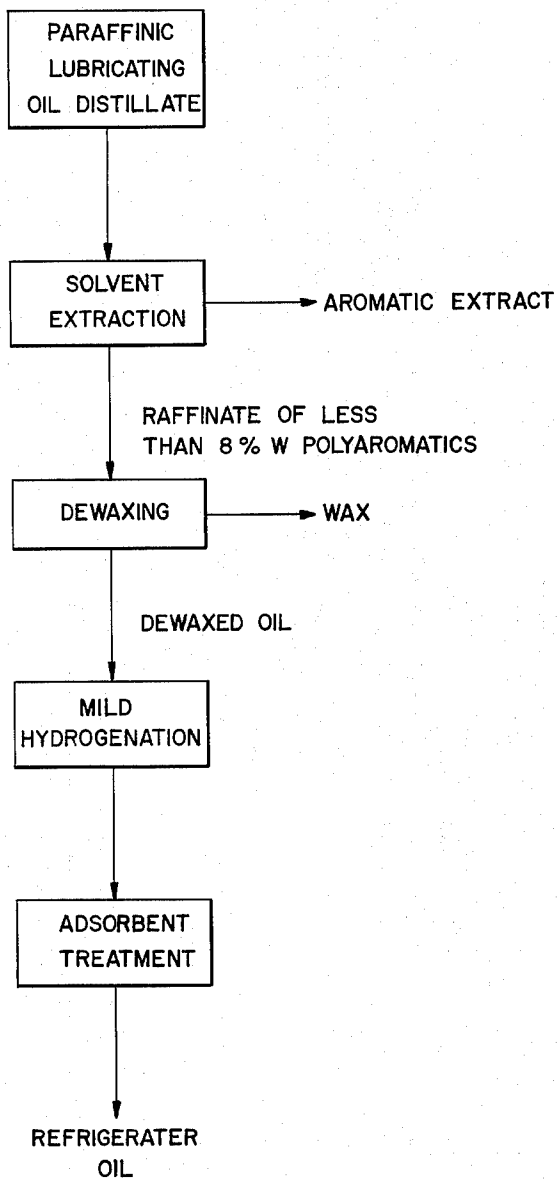
Dec. 21, 1965

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3,224,955

LUBRICATING OIL PROCESS

Filed Dec. 18, 1962



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LUBRICATING OIL PROCESS

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Filed Dec. 18, 1962, Ser. No. 245,384
5 Claims. (Cl. 208—28)

This invention relates to a process for preparing lubricating oils and more particularly it relates to a process for preparing lubricating oils for refrigeration units.

Refrigerators, food freezers, air conditioners and the like, except those that are motorless, have compressors which compress the refrigerant. The most commonly used refrigerants are those which are immiscible with the lubricant, such as ammonia, sulfur dioxide and the like and those which are miscible with the lubricant, such as halogen type, for example, methylchloride and chlorofluoro carbons (Freons). The Freons, such as Freon 12 (dichloro-difluoro methane), have become widely used in the industry.

When refrigeration units are assembled, the lubricating oil is hermetically sealed inside the equipment. Here it is in contact with the refrigerant and the metals and other materials of construction during the life of the mechanism. As the totally enclosed units are to provide a satisfactory service for a long period of time, the lubricant should be oxidation stable, non-sludging and non-corrosive. The oil should be sufficiently soluble in liquid Freon to properly lubricate the compressor bearings and other moving parts. In addition, the oil carried over to the low temperature side of the unit should not separate and coat heat exchange surfaces or plug restrictor valves. In the high temperature, high pressure zone of the unit, the thermal stability of the oil—Freon mixtures in the presence of metal is of great concern. These performance characteristics are the most critical for the refrigerator oil.

Demand for refrigerator oils has been met by drastic refining of lubricating oils such as by severe acid treating and clay contacting. Such refining methods are highly expensive, present disposal and handling problems, and generally result in a low yield of finished oil.

It has been found, in accordance with the present invention, that satisfactory refrigerator oils can be prepared by extracting mineral lubricating oil distillate to a polyaromatic content less than about 8% by weight, mildly hydrotreating the lubricating oil raffinate to desulfurize the oil and then subjecting the hydrogenated oil to a moderate clay treatment. The drawing is a block flow diagram which sets forth operational steps in the practice of this invention.

The starting material is a straight-run mineral oil distillate, preferably from a paraffinic type crude oil. Paraffinic oils produce lubricating oils of high viscosity index (HVI) which are desired because of the extremes of temperatures at which a refrigerator oil must function in service. The distillates are produced by fractional distillation, generally under vacuum, of the crude oil into fractions of varying viscosity (Saybolt Universal at 100° F.) and boiling ranges, such as 100 distillate, 250 distillate, heavy (700) distillate, and short residue. The distillates are generally refined separately to provide base stocks which can be blended to give an oil of the desired finished properties.

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The lubricating oil distillate starting material is subjected to an aromatic extraction process with a solvent selective for aromatics, such as furfural, SO₂, phenol and the like. Extraction is usually conducted at relatively low temperatures of about 80–200° F. and solvent to feed volumetric ratios of 0.5–5. Polyaromatic content of distillate fractions generally ranges from about 15–30% by weight. In the process of the invention the extraction should be severe enough to reduce polyaromatic content of the raffinate to less than about 8% by weight, preferably less than 5% by weight, the extraction conditions employed to achieve this depth of extraction depending upon the particular distillate feed and solvent used. Solvent extraction processes are well known and are practiced commercially, therefore detailed discussion should not be required. Acidic solvents such as phenol are preferred as they tend to remove more of the basic nitrogen compounds from the lubricating oil distillates.

Extraction removes unstable constituents from the oil, primarily polyaromatics and nitrogen, sulfur, and oxygen compounds, usually in an aromatic structure. Resistance of the oil towards oxidation and sludging is improved. However, the presence of mono-aromatics in the oil is desired to give the oil oxidation stability. By removing polyaromatic and nitrogen compounds, the extraction improves viscosity index of the oil and improves susceptibility of the oil to oxidation inhibitors.

With paraffinic type crudes, dewaxing is required to remove waxy components, which thereby improves the pour point of the oils. Raffinate from the extraction process can be subjected to any suitable dewaxing operation. Dewaxing processes employed commercially employ solvents such as propane, methyl-ethyl-ketone (MEK)/benzene, and the like. Pour point of the dewaxed oil is preferably below about 10° F. Alternatively, dewaxing may precede solvent extraction.

The dewaxed raffinate is subjected to a mild hydrodesulfurization wherein sulfur and oxygen compounds are hydrogenated while the hydrocarbons remain substantially unaffected, i.e. virtually no cracking of the oil or hydrogenation of aromatics present in the oil. Viscosity index of the oil may be slightly increased by the mild hydrotreatment. The oil may be in either the gas or the liquid phase during hydrogenation, a very suitable method being trickle phase hydrogenation wherein the liquid oil is caused to flow through a bed of catalyst in the presence of hydrogen. In general, the hydrogenation is carried out at a temperature of 550° to 700° F., a pressure of 450 to 1500 p.s.i.g., a gas discharge rate of 250–1200 standard cubic feet of hydrogen per barrel of oil, and a liquid hourly space velocity of about 1 to 4. Under the mild conditions, hydrogen consumption will be about 20–250 standard cubic feet/barrel of oil and sulfur removal will be about 50–75% complete. More severe hydrogenation, i.e. low space velocities, high pressures and high temperatures, would increase sulfur and nitrogen removal, hydrogenation of aromatics, and hydrogen consumption, but would be considerably more expensive.

Suitable hydrodesulfurization catalysts are oxygen or sulfur containing compounds such as the oxides and the sulfides of metals of Group 6 and Group 8 of the Periodic Table. Especially preferred are molybdenum oxide together with cobalt oxide and/or nickel oxide, or tungsten sulfide and nickel sulfide. The catalysts are preferably supported on a carrier such as active carbon, kieselguhr,

silica, alumina, and the like. The catalyst may be used in the form of tablets, pellets, extrudates and the like. Hydrodesulfurization catalysts are well known and many are available commercially. A suitable hydrogenation method is described, for example by Hoog, U.S. Patent 2,608,521, issued August 26, 1952.

In the hydrodesulfurization, a minor amount of low boiling components is produced which results in a lowering of the flash point of the oil. It may be necessary to remove these low boiling components to satisfy flash point requirements of the finished oil. This can be done by means of steam-stripping or distillation, preferably under reduced pressure.

Following the hydrodesulfurization, the oil is moderately treated with a solid adsorbent such as fuller's earth and activated clays. Common adsorbents are for example attapulgite and montmorillonite and the acid activated clays such as bentonite, bauxite and alumina. Suitable adsorbents are Porocel and Filtrol. The treatment can be effected at elevated temperatures, for example, from about 200–500° F. When stripping of hydrodesulfurized oil is employed, it is generally desired to pass the stripped oil at normal stripper bottoms temperatures through a percolation filter containing the adsorbent. Contact filtering with moderate clay dosages can be employed if desired. The quantity of adsorbent used generally lies between 0.5 and 10% by weight, preferably between 1 and 5% by weight, calculated on the oil treated. In practice, the various distillate fractions will often be blended in the desired proportions prior to the adsorbent treatment.

Hydrodesulfurization of the oil results in a more effective adsorbent treatment since sulfur and oxygen compounds are removed in the hydrotreating operation which would otherwise interfere by forming viscous residues on the adsorbent. Moreover, although little or no nitrogen compounds are removed in the hydrodesulfurization, the hydrotreatment apparently promotes nitrogen base formation resulting in increased denitrification in adsorbent treatment.

Removal of traces of nitrogen compounds, particularly basic nitrogen compounds, is essential to obtain satisfactory chloride ion stability test results for refrigerator oils. The chloride ion stability test is designed to stimulate conditions in service where oil, Freon and materials of construction are in contact with one another during the operating life of the refrigerator unit. Test oil, Freon 12, steel and copper in prescribed amounts are heated together in a sealed tube at test temperature, generally 400° F. After a given time the tube is cooled and opened and the oil is examined for sludge, color, and the amount of chloride ion formed. A minimum of chloride ion is desirable since chloride accelerates rusting, metal corrosion, and deterioration of organic materials, e.g. insulation.

If desired, suitable additives such as oxidation inhibitors, anti-foam agents and the like can be incorporated in the treated oil to improve characteristics of the oil. The additives should be oil soluble and non-sludge forming. Oxidation inhibitors such as the phenolic type, e.g. 2,6-ditertiarybutyl-4-methylphenol, are preferred, since nitrogen compounds, such as the amine type, can adversely affect chloride-ion stability of the oil.

Viscosity of the final lubricating oil can be within a wide range, depending upon the particular service and preferences of the refrigeration unit manufacturer. Viscosity of lubricating oil in refrigerator service is usually about 500 SSU at 100° F., although oils of a viscosity as low as 80 SSU at 100° F. can be used if desired. Oils having a viscosity of 1000 SSU at 100° F. and higher are desired for air conditioning units. Viscosity index of the final oils is at least about 85 and preferably at least 90.

EXAMPLE

Long residue from the topping of lube crude is vacuum distilled into 100 distillate, 250 distillate, heavy (700) dis-

tillate, and short residue. The 250 and heavy distillates are extracted with phenol, solvent to feed volumetric ratio of about 1.2 and 2.4, respectively, and the raffinates obtained are dewaxed with methyl-ethyl-ketone/toluene (app. 60% MEK, 40% toluene) at solvent to oil ratios of about 2.3 and 3.5 respectively. Typical properties of the extracted and dewaxed distillates are given in Table I.

Table I

| | HVI 250 Distillate | HVI Heavy Distillate |
|---------------------------|--------------------|----------------------|
| Gravity, ° API | 28.4 | 28.8 |
| Color, ASTM D-1500 | 0.5 | 0.5 |
| Viscosity, SSU at 100° F. | 250 | 693 |
| Viscosity, SSU at 210° F. | 49.5 | 72.7 |
| Viscosity index | 92.2 | 92.4 |
| Flash Point, °C, ° F | 440 | 370 |
| Pour Point, ° F | 10 | 5 |
| Nitrogen, p.p.m. | 24 | 13 |
| Sulfur, percent | 0.04 | 0.09 |

Several blends of the dewaxed distillates were prepared, each blend containing about 80–85% w. heavy distillate and having a viscosity of about 500 SSU at 100° F. A typical blend has the following aromatic hydrocarbon content, by ultraviolet analysis (mol. wt. 510–520):

| | percent wt. |
|----------------|-------------|
| Monoaromatics | 9.8 |
| Diaromatics | 2.0 |
| Triaromatics | 0.3 |
| Tetraaromatics | 0.2 |

Thus, the polyaromatic content was about 2.5% wt. The various blends were subjected to clay contacting or percolation with or without a previous hydrotreatment over nickel molybdenum on alumina hydrogenation catalyst. Nitrogen content and chloride ion test results are given below in Table II. The chloride ion test was determined on sample containing 0.5% w. oxidation inhibitor (2,6-ditertiarybutyl-4-methylphenol) and 5 p.p.m. antifoam agent (Dow Corning Fluid, Type 200).

Table II

| No. | Treatment | Nitrogen, p.p.m. | | Chloride Ion after 2 weeks at 400° F. mg. |
|-----|---|------------------|-------|---|
| | | Total | Basic | |
| 1 | Untreated blend | 31 | 11 | |
| 2 | Clay contacted, 30 lb. Filtrol 88/bbl. | 9 | <1 | 10 |
| 3 | Percolated over Porocel at 210° F. | 27 | 2 | 147 |
| 4 | Hydrotreated 675° F., 450 p.s.i.g., 2.5 LHSV | 34 | 11 | 425 |
| 5 | Hydrotreated 675° F., 450 p.s.i.g., 1.25 LHSV | 15 | 4 | 177 |
| 6 | Hydrotreated 675° F., 550 p.s.i.g., 1.25 LHSV | 21 | 5 | 149 |
| 7 | No. 4 percolated over Porocel at 210° F. | 8 | <1 | 5.2 |
| 8 | No. 4 clay contacted, 30 lb. Filtrol 88/bbl. | 10 | <1 | 3.6 |

As shown in Table II, simple percolation (No. 3) of extracted and dewaxed oil is far less effective than clay contacting (No. 2). Similarly, mild hydrotreatment is also ineffective (Nos. 4–6). However, mild hydrotreatment prior to clay treatment (Nos. 7–8) has markedly improved chloride ion test results. In addition, a comparison of numbers 3 and 7 shows that hydrotreatment facilitates denitrification by percolation clay treatment. The difference in chloride-ion reactivity of oils having a basic nitrogen content below the detectable level of 1 p.p.m. is presumed to be related to the presence of pyrrole, indole, or carbazole type compounds which are too weakly basic to be detected by the perchloric acid-acetic acid reagent used to measure basic nitrogen content.

I claim as my invention:

1. A process for the production of refrigerator oil which comprises extracting a paraffinic lubricating oil distillate

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with a solvent selective for aromatics to obtain a raffinate having a polyaromatic content less than about 8% by weight, dewaxing the raffinate, catalytically hydrotreating the dewaxed raffinate under mild conditions of about 550° to 700° F., about 450 to 1500 p.s.i.g., and about 1 to 4 liquid hourly space velocity, and contacting the hydrotreated oil with a solid adsorbent.

2. A process for the production of refrigerator oil which comprises extracting a paraffinic lubricating oil distillate with a solvent selective for aromatics to obtain a raffinate having a polyaromatic content less than about 8% by weight, dewaxing the raffinate, catalytically hydrotreating the dewaxed raffinate under mild conditions of about 550° to 700° F., about 450 to 1500 p.s.i.g., and about 1 to 4 liquid hourly space velocity, and percolating the hydrotreated oil through a solid adsorbent.

3. A process for the production of refrigerator oil which comprises extracting a paraffinic lubricating oil distillate with a solvent selective for aromatics to obtain a raffinate having a polyaromatic content less than about 8% by weight, dewaxing the raffinate, catalytically hydrotreating the dewaxed raffinate under mild conditions of about 550° to 700° F., about 450 to 1500 p.s.i.g., and about 1 to 4 liquid hourly space velocity, and con-

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tacting the hydrotreated oil with between about 0.5 and 10% by weight of a solid adsorbent.

4. A process for the production of refrigerator oil which comprises extracting a paraffinic lubricating oil distillate with an acidic-solvent selective for aromatics to obtain a raffinate having a polyaromatic content less than about 8% by weight, dewaxing the raffinate, catalytically hydrotreating the dewaxed raffinate under mild conditions of about 550° to 700° F., about 450 to 1500 p.s.i.g., and about 1 to 4 liquid hourly space velocity, and contacting the hydrotreated oil with a solid adsorbent.

5. The process according to claim 4 wherein the solvent is phenol.

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