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# ADHESIVE PETROLEUM LUBRICANT

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This invention relates to adhesive lubricant compositions and to the method for their preparation.

The primary object of this invention is to provide an adhesive lubricant containing a certain petroleum by-product adapted to impart thereto the stringiness and adhesiveness necessary for holding the lubricant to metal surfaces.

A second object of this invention is to provide an adhesive lubricant suitable for curve greases, wire rope lubricants, and the like wherein extremely unctuous properties are of primary importance.

A third object of this invention is to provide adhesive lubricants containing up to 20 per cent or more of a certain petroleum by-product derivable from the new delayed coking operation, which petroleum by-product is stringy, unctuous, adhesive, non-crystalline, and contains appreciable quantities of resinous petroleum hydrocarbons with smaller amounts of hydrocarbons classifiable as asphaltenes and waxes.

Further objects of this invention will become apparent as the description thereof proceeds.

Briefly, the present invention relates to the discovery that the petroleum by-product which separates from the steam condensate produced during the steaming of the porous coke mass that results from the delayed coking of reduced crude oils has valuable properties when compounded with other petroleum products, such as any residuum from the distillation of petroleum oils, tube still bottoms, or asphalt with or without certain alkali metal soaps, to form greases and lubricants suitable for use where adherence to metal surfaces is desirable.

Before describing specific embodiments of the invention, some statements concerning petroleum by-products in general are in order.

During the distillation, thermal degradation, cracking, or coking of hydrocarbon oils for the purpose of obtaining therefrom gasolines, lubricating oil portions, and fuel oils, certain petroleum by-products are accumulated which may contain asphaltenes, neutral resins, residual oils, and waxes. These petroleum by-products are generally used as or blended with fuel oil or cracking stock. The physical and chemical properties of these by-products vary widely depending on the conditions under which they are formed.

In some instances, uses have been found for certain normally solid and non-tacky petroleum by-products which contain high proportions of aromatics with two, three, or four condensed aromatic rings with or without substituent alkyl groups. These materials do not easily oxidize to varnish or resinous materials of asphaltic nature and are known inhibitors against the oxidation of lubricating oils. One such product is described in United States Patent 2,281,894 by George von Fuchs, et al. Von Fuchs discloses the liquid phase cracking of gas oil or like hydrocarbons under conditions to produce coke instead of residual black fuel oil and under temperatures usually in the order of 865° to 895° F. The vapors leaving the coking chamber are fractionated leaving a heavy fraction called coking cycle stock. The cracking reaction chamber, which operates at high pressures is next blown with steam to cause the vaporization of additional aromatic material, called coke blow down oil. The coking cycle stock and aromatic coke blow down oil are described by von Fuchs as having the ability to inhibit the oxidation of refined mineral lubricating oils, and are non-tacky, non-adhesive, liquid or crystalline aromatic by-products.



The present invention is based on the discovery of a valuable property of another type of petroleum material, which is a by-product of the new delayed coking operation, having entirely different properties from the aromatic petroleum by-product above referred to. This product is obtained in the following manner. Yates crude oil is fractionated to drive off gasoline, virgin naphtha, and kerosene, producing about 40 per cent reduced crude. West Texas crude, containing variable amounts of sulfur compounds, is similarly treated to yield a 30 per cent reduced crude. The two reduced crudes are combined and fed to a feed accumulator, where temperatures of about 550° F. obtain. From the feed accumulator, the mixture of hot reduced crudes pass to a partial vaporizor coil where temperatures of about 750° F. are maintained. The purpose of this heating step is to drive out additional gas oil which is allowed to vaporize in a fractionating tower. The bottoms from this tower, at about 730° F., are called coking coil charge and comprise a mixture of straight run asphalt plus heavy partially cracked recycle stock. These bottoms are passed through a coking coil wherein short residence time and high velocities are maintained to vaporize 60 to 70 per cent of the bottoms under conditions of low pressure drop to avoid the accumulation of carbon therein and insure early vaporization. The exit temperature from the coking coil will be about 915° F. with a pressure of about 30 p. s. i. g. The vaporized bottoms then pass immediately to the coking drums, which are usually operated in pairs. Within the coking drums, the asphaltic hydrocarbons gradually coke and the light products vaporize off. The coke drum product from the top of the coking drums is recycled back to the fractionating tower. This coke drum product contains cracked gases, gasoline, light distillate, heavy distillate, and heavy recycle. After a certain time cycle, the coke drum is filled with coke and ready for depressuring. This step is carefully conducted to prevent carry-over of coke with the light oils which are released thereby and collected as blow down oil. Steam is then introduced into the bottom of the coking drum and the remaining materials in the coke are distilled out. The steam condensate from the steam treatment is conducted to suitable containers where it can cool. During the cooling operation, considerable water separates leaving so-called "wax tailings."

The mechanism of the delayed coking reaction has been a matter of speculation. As the coking coil charge enters the coke drum, due to its high latent heat content, a succession of dehydrogenations and splitting off of light hydrocarbons from the coking coil charge begins. The mass that is left by this process is not all elemental carbon but a mixture of carbon and certain hydrocarbons of very high molecular weight and having a high carbon to hydrogen ratio. As the destructive distillation or coking reaction proceeds, the coking coil charge passes through the asphalt and pitch stage to finally decompose into a porous mass of coke. The depressuring step releases gradually any occluded hydrocarbons, as has been described. The wax tailing by-product separated from the steam condensate is a stringy, adhesive, non-crystalline mass which is very difficult to handle and presents a disposal problem.

These wax tailings from a new delayed coking operation have been found to contain a high concentration of resinous hydrocarbons and appreciable concentrations of hydrocarbons classifiable as asphaltenes. The resinous and asphaltic compounds contained therein, when subjected to slight oxidation conditions, produce a heavy varnish and, consequently, are unsuited for use as oxidation inhibitors in lubricating oils subjected to such conditions. Wax tailings, if added to lubricating oils, would raise the carbon residue content of the oil and produce a poor motor oil. However, this extremely unctuous by-product has been found to form good lubricants where adherence to metal surfaces under various conditions is important when compounded with such ingredients as tube still bottoms, asphalts, and waxes, including petrolatum, with or without alkali earth metal soaps, as before stated.

The physical and chemical properties of wax tailings from the delayed coking operation are dependent somewhat on the nature of the crude source and upon the conditions of the coking process. A Mid-Continent or East Texas crude may be used as the source material. Although the crude sources used to demonstrate the preparation of the wax tailings contained an appreciable amount of sulfur compounds making them classifiable as sour crudes, it is not necessary that sour crudes be used as starting materials. Mixtures of reduced Mid-Continent crude and reduced intermediate sweet East Texas crude may be used as starting materials.

It is customary to use the reduced crude at the temperature at which it is withdrawn from the bottom of the fractionating tower, although such practice is not always necessary. These temperatures may range from 700° to 760° F. with pressures at atmospheric or super atmospheric. In a typical operation at 6,800 BPSD (barrels per stream day), a mixture of 3,000 BPSD of 30 per cent reduced Mid-Continent or Yates crude and 3,800 BPSD of 40 per cent East Texas crude may be fed to the feed accumulator. The combined feed ratio through the coking coil may be approximately 63 and the pressure therein may be from 10 to 40 pounds per square inch.

The residence time within the coking coil may be expressed in different terms. One convenient method is to express the residence time as the number of barrels of cold crude feed charged per cubic foot of radiant tube volume in the coking coil. Thus, with a furnace having 68 tubes, each 23 feet long, 5 inch outside diameter, and with 0.375 inch wall thickness, the total radiant tube volume in cubic feet is 153.4. At 6,840 BPSD the number of barrels charged per cubic foot of radiant tube volume is about 44.5. This value is variable. For example, if a heavier crude than a 40 per cent reduced crude is used, this ratio may fall to 30 or 35 and, if a lighter reduced crude than 30 per cent is used, it may be raised to 50 or 55.

The inlet temperature to the coking drum is about 900° to 930° F. under pressures of about 30 pounds per square inch and the outlet temperature may be about 820° to 840° F., average about 835° F. under 20 pounds per square inch. Very little pressure drop occurs within the coking drum.

Generally, two or more coking drums are employed and, while one is on stream, the other is being de-coked. The effluent products from the coking operation are fractionated to yield various cuts including gasoline, naphtha, fuel oil, and coking recycle stock. When two coking drums are used, the operating cycle for each may be 24 hours. During the last two to four hours of the on-stream cycle of one drum, part of the hot effluent therefrom may be conducted into the second drum, which has been de-coked, for the purpose of heating the second coking drum to operating temperature before it is put on stream.

At the end of the on-stream cycle of one drum, the introduction of heated topped crude therein is terminated and the mechanical de-coking operation begun, after which the steam blow down step takes place.

The wax tailings referred to herein contain neutral resins which are non-crystalline, sticky solids when recovered from a delayed coking operation conducted under the conditions described. They are soluble in aromatic solvents. These resins are adsorbed by silica gel and desorbed by alcohol. Quantitative analysis indicates the presence of a very complex structure including fused rings, as shown by the high carbon residue content. The carbon to hydrogen ratio is greater than 13 and the molecular weights may go as high as 2,000. The densities are above 1.0. It has been postulated that these neutral petroleum resins present in wax tailings serve as dispersing agents for the higher asphaltenes in oils. A typical wax tailing product so obtained has a Hubbard specific gravity at 60° F. of 1.118; about 2.4 per cent total sulfur is present and the per cent Conradson carbon residue is 9.59. The total ash content is 0.02%, and the Wijs iodine number is 61.8.

Petroleum resins are present in wax tailings in amounts of at least about 30 percent. The petroleum resins contain about 89.7 per cent carbon, 6.4 per cent hydrogen, and 2.94 per cent sulfur, are greenish-black, and extremely sticky. Asphaltenes, though present in the wax tailings, amount to only about 2.0 to 4.0 per cent of the composition. On analysis, the asphaltenes show 89.9 per cent carbon, 5.6 per cent hydrogen, and 2.3 per cent sulfur, and are a brown powder. The dewaxed mineral oil obtainable in small amounts from the wax tailings is a dark green viscous liquid having an API gravity at 60° F. of 3.0, a viscosity of 102.6 SUS at 210° F., 88.8 per cent carbon, 8.2 per cent hydrogen, and 2.23 per cent sulfur. The viscosity index is minus 376. The small amount of wax separatable from the tailings shows on analysis 86.5 per cent carbon, 12.1 per cent hydrogen, and 1.06 per cent sulfur. The amount of asphaltenes present in the wax tailings may be about 4 per cent by weight, the petroleum resin content about 35 per cent by weight, and the wax content preferably under about 2 per cent by weight.

Sulfur in combined form is present in each of the ingredients making up the wax tailings. The total sulfur content of a wax tailing which was found to be preferred for formulating curved greases and wire rope lubricants, in accordance with this invention, is about 2.4 per cent by weight.

The above described wax tailings containing large amounts of neutral resins and small amounts of asphaltenes, as obtained from the delayed coking operation, are especially suited to impart adhesive qualities to residuum lubricating compositions. For this purpose, blends of residua and greases containing 0.10 to 20 per cent of the stringy product may be used. The product may also be used to blend with asphaltic materials to impart thereto the property of adhering to aggregate earthy materials. The wax tailings may also be used in slushing compounds. If it is desired that the black color be removed, this may be done by ordinary refining process as by treatment with a high boiling naphtha and filtration through fuller's earth or other adsorptive material and removal of the solvent by distillation. This refined product is suitable for use in lighter colored lubricants where color specifications are important.

Wax tailings when compounded with tube still bottoms, asphalt, petrolatum, and certain additives, form adhesive lubricating compositions including curve greases and wire rope lubricants. Typical compositions by weight per cent are as follows:

*Curve greases*

| | Per cent |
|---|---|
| Formula No. 1: | |
| Tube still bottoms | 95–80 |

*Curve greases*—Continued

| | Per cent |
|---|---|
| Wax tailings | 5–20 |
| Formula No. 2: | |
| Calcium rosinate | 10 |
| Tube still bottoms | 85 |
| Wax tailings | 5 |
| Formula No. 3: | |
| Tube still bottoms | 90–60 |
| Asphalt | 0–30 |
| Wax tailings | 10 |

*Wire rope lubricants*

| | |
|---|---|
| Formula No. 1: | |
| Asphalt | 70 |
| Wax tailings | 15 |
| Petrolatum | 15 |
| Formula No. 2: | |
| Petrolatum | 90 |
| Wax tailings | 10 |

In the above formulations, specific straight run residua as tube still bottoms and asphalt are used. These products are obtained by distilling petroleum oils to drive off all readily volatile constituents leaving residua of this nature. Any residuum from the distillation of petroleum oils may be used as an ingredient of the compositions of the invention. Tube still bottoms of any viscosity may be used depending on the end physical characteristics of the grease or lubricant that are desired. Tube still bottoms having viscosities at 210° F. of 400 to 700 are useful for this purpose.

A specific example of tube still bottoms suitable for use in compositions compounded in accordance with this invention is Van Zandt tube still bottoms having the following tests:

*Tests on Van Zandt tube still bottoms*

| A. P. I. Gravity | Flash (° F.) | Fire (° F.) | S. U. S. Viscosity at 210° F. | Min., Pour (° F.) |
|---|---|---|---|---|
| 14.5 | 560 | 635 | 614 | +55 |

This particular sample of Van Zandt tube still bottoms had an IBP of 855° F. and in its production the cutting point in the distillation of the crude was 850° F. (when corrected to atmospheric pressure). An example of an asphalt suitable for the purposes of this invention is a blown asphalt having a ring and ball melting point of 165–185° F.

Residua from the cracking of fuel oil or destructive distillation processes may be used. Although the wax tailings cannot be blended with lubricating oil fractions for the purpose of inhibiting the oxidation thereof during use because of their high content of easily oxidizable resins, this does not exclude the incorporation of mineral lubricating oils as part of the compositions. A residuum of high viscosity can be blended with a mineral lubricating oil to yield a mixture having viscosity properties approaching those of a curve grease or wire rope lubricant. This mixture is then blended with wax tailings with or without a cheap source of soap, as calcium rosinate or any other metal soap, to yield a grease having the desired unctuous and adhesive properties along with good gel structure due to its soap content.

The above formulas are subject to some variation without departing from the scope of the invention. Although the invention has been described and illustrated by specific examples, the only limitations thereon appear in the appended claims.



The term "wax tailings" as used throughout this specification is not meant to include the petroleum products derived by propane or butane solvent extraction or precipitation methods. Nor is it meant to include the normally solid non-tacky, oily, or crystalline material called "coke blow down" or unrefined blow down oil obtained as described in the von Fuchs patent, supra.

What is claimed is:

1. A lubricating composition characterized by its adhesiveness to metal surfaces, comprising a major portion of a residuum from the distillation of a petroleum oil and a small amount of unctuous, stringy, non-crystalline wax tailings having an asphaltene content of not above 4 per cent by weight and a petroleum resin content of at least about 30 per cent by weight, a wax content of under 2 per cent by weight, and a sulfur content of about 2.4 per cent by weight.

2. The composition in accordance with claim 1 in which from 0.1 to 20 per cent by weight of said wax tailings are present in the composition.

3. A lubricating composition in accordance with claim 1 in which the residuum comprises tube still bottoms and said wax tailings are present in an amount from about 5 to 20 per cent by weight.

4. A lubricating composition in accordance with claim 3 in which the tube still bottoms have a viscosity of about 400 to 700 SUS at 210° F.

5. A curve grease composition containing a major portion of tube still bottoms having an API gravity of about 14.5, a viscosity of about 614 SUS at 210° F., and a minimum pour point of 55° F., and from 5 to 20 per cent by weight of unctuous, stringy, non-crystalline wax tailings having an asphaltene content of not above 4 per cent by weight, a petroleum resin content of at least about 30 per cent by weight, a wax content of under 2 per cent by weight, and a sulfur content of about 2.4 per cent by weight.

6. A curve grease composition containing a major portion of tube still bottoms having an API gravity of about 14.5, a viscosity of about 614 SUS at 210° F., and a minimum pour point of 55° F., about 10 per cent by weight of calcium rosinate and about 5 per cent by weight of unctuous, stringy, non-crystalline wax tailings having an asphaltene content of not above 4 per cent by weight, a petroleum resin content of at least about 30 per cent by weight, a wax content of under 2 per cent by weight, and a sulfur content of about 2.4 per cent by weight.

7. A curve grease composition comprising a major portion of tube still bottoms having an API gravity of about 14.5, a viscosity of about 614 SUS at 210° F., and a minimum pour point of 55° F., from 1 to 30 per cent of asphalt, and from about 10 per cent by weight of unctuous, stringy, non-crystalline wax tailings having an asphaltene content of not above 4 per cent by weight, a petroleum resin content of at least about 30 per cent by weight, a wax content of under 2 per cent by weight, and a sulfur content of about 2.4 per cent by weight.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 1,917,875 | Davis | July 11, 1933 |
| 2,074,039 | Zimmer et al. | Mar. 16, 1937 |
| 2,170,495 | Fischer | Aug. 22, 1939 |
| 2,211,254 | Chittick | Aug. 13, 1940 |
| 2,211,921 | Brunstrum et al. | Aug. 20, 1940 |
| 2,378,818 | Zimmer | June 19, 1945 |