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GREASE COMPOSITIONS

Richard A. Butcosk, Westmont, N.J., assignor to Mobil Oil Corporation, a corporation of New York

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This invention relates to grease compositions and, in one of its aspects, relates to grease compositions containing improved lubricating oil vehicles. More specifically, in this aspect, the invention relates to grease compositions, containing improved lubricating oil vehicles, of improved endurance life, low-temperature torque and anti-wear properties.

Prior to the present invention, a wide variety of vehicles have been employed in grease formulations, and have included such fluids as acid-treated mineral oils, solvent-refined mineral oils, esters and silicones. Greases containing these fluid vehicles have successfully performed in many fields of operations; however, each type has also exhibited certain specific limitations such as volatility at high temperature, lack of load-carrying ability, or relatively low viscosity indexes, and affecting their endurance life and anti-wear properties.

It is, therefore, an object of the present invention to provide new and improved grease compositions.

Another object of the invention is to provide grease compositions having improved endurance, low-temperature torque and anti-wear properties.

Still another object of the invention is to provide a method for producing the aforementioned improved grease compositions.

Other objects and advantages inherent in the invention will become apparent to those skilled in the art from the following more detailed description.

In accordance with the present invention, new and improved grease compositions are obtained which contain a specific type of lubricating oil vehicle. In general, this vehicle comprises a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction to produce a product which contains a relatively high boiling lubricating oil fraction. This high boiling oil fraction is separated from the product, and is resolved into a plurality of oil fractions of different boiling ranges. Thereafter, portions of these resolved fractions are combined to produce the desired lubricating oil vehicle, which is employed in conjunction with any conventional gelling or thickening agent to produce a novel and improved grease composition.

More specifically, in preparing the aforementioned lubricating oil vehicle, a relatively high molecular weight residual material comprising a resinous extract and aromatics, either with or without waxy constituents, and derived from a relatively high boiling hydrocarbon fraction, particularly an asphalt-free or deasphalted petroleum residuum, is passed with hydrogen to a hydrocracking zone maintained under relatively severe hydrocracking conditions. During the hydrocracking step, the resins, aromatics and waxy constituents present, are upgraded to quality materials comprising lubricating oil, fuel oil and naphtha-boiling range materials. The thus-prepared lubricating oil boiling range material is thereafter separated by fractionating under vacuum conditions into desired viscosity boiling range product fractions, and, if necessary, thereafter dewaxed to provide specific pour point lube oils, suitable for use as grease vehicles.

In this connection, it has been found, that when a waxy bottom product having an initial boiling point of at least about 600° F. is recovered from the total liquid product effluent of the hydrocracking step and further separated into a plurality of individual boiling range

fractions, dewaxing conditions for removing wax from the individual fractions need not be as severe as would be normally required. Thus, it is found that in subjecting the particular fractions thus obtained to 0° F. dewaxing conditions, there is produced a 0° F. pour point oil rather than a 20° F. pour point oil, as would be normally expected. In general, and particularly when the feed material is employed containing waxy constituents, it is preferred to employ relatively lower product dewaxing temperatures, namely from about 0° F. to about minus 80° F., to produce oils having a pour point from about −10° F. to about 25° F.

In a more particular aspect, it has been found that a resin extract either with or without waxy constituents and recovered from a cylinder stock in the preparation of Bright stock may be hydrocracked in the presence of hydrogen and a hydrocracking catalyst maintained at a temperature in the range of from about 720° F. to about 850° F.; a hydrogen partial pressure in the range of from about 800 p.s.i.g. to about 3,000 p.s.i.g.; a space velocity in the range of from about .05 to about 1.5 v./v./hour and preferably below .8 v./v./hour, suitable for preparing the lubricating oil vehicles of the improved grease formulations.

Although a paraffin base crude is preferred as the starting material for preparing the lubricating oil vehicle, other feed stocks may be used, including relatively high boiling deasphalted residual fractions from which a resin extract either with or without waxy material may be obtained. Accordingly, the starting petroleum charge stock may be any deasphalted petroleum residual fraction from which paraffinic and naphthenic constitutents are removed having resinous and/or aromatic constituents therein, and which may or may not have been subjected to partial or complete dewaxing at a temperature of about 0° F. This material either with or without wax constituents is the preferred hydrocarbon feed.

In a more particular aspect, destructive hydrogenation. and/or hydrocracking conditions are sufficient to convert a resin extract containing feed material, and those conditions embody relatively severe carbon-carbon bond cleavage hydrocracking conditions in the presence of a gas exerting a hydrogen total pressure of at least about 1,500 p.s.i.g. and preferably about 2,500 p.s.i.g.; a temperature below about 810° F. and preferably about 770° F., while employing a hydrogen to a hydrocarbon feed ratio of at least about 5 to 1 mole ratio and a space velocity below about .8 v./v./hour and preferably below about .3 v./v./hour. That is, a non-isomerizing hydrocracking catalyst of the type such as CoMoZr.Si may be employed or a hydrocracking catalyst exerting an isomerizing effect such as a Pt-Al catalyst promoted with from about 3–7 percent fluorine may be employed, particularly when the resin extract contains appreciable wax.

The catalyst which may be employed in the hydrocracking step may be substantially any of the known catalysts which promote the hydrocracking reaction desired. It is preferred, however, to employ an acidic hydrocracking catalyst promoted with a Group VIII metal component. Other suitable hydrocracking catalysts include the oxides and sulfides of the metals of Group VI or mixtures thereof such as, chromium sulfide, molybdenum sulfide, tungsten sulfide and the like; oxides and sulfides of Group VIII or mixtures thereof such as iron, cobalt, nickel, palladium, platinum, rhodium, osmium, iridium, or mixtures of one or more components selected from Groups VI and VIII of the Periodic Table. These materials and mixtures thereof may be deposited on a suitable carrier material, preferably, on acidic carrier materials such as silica alumina, silica zirconium, and alu-

mina promoted with boria and/or a halogen promoter such as bormine, chlorine, and fluorine.

The total liquid product obtained from the hydrocracking process herein described is separated under atmospheric distillation conditions to obtain a bottoms fraction having an initial boiling point of at least about 600° F. which is thereafter separated under vacuum distillation conditions to obtain a plurality of separate boiling range fractions suitable for blending to desired lube oils. Depending on the producer, the overhead liquid hydrocracked product may be separated to recover a fuel oil from a light and heavy naphtha boiling range product.

In a preferred embodiment of this invention, the waxy bottoms product having an initial boiling point of about 600° F. is vacuum retorted or separated into a plurality of separate boiling range fractions including a heavy bottoms fraction as shown in Table I presented below and having the physical properties indicated.

TABLE I

Cut No.	1	2	3	4	5	6	7	8
Boiling Range, ° F.	660-825	825-870	870-925	925-995	995-1, 045	1, 045-1, 100	1, 100-1, 135	1, 135+
Waxy Fractions: Pour Point, ° F.	20	30	35	50	60	70	65	5
Viscosity:								
KV at 100° F.	7.7	9.4	11.2		23.3	38.9	67.6	607
KV at 210° F.	2.2	2.6	2.9	3.6	4.7	6.7	9.6	44.5
SSU at 100° F.	51.1	56.9	63.3		112	181	313	2,813
SSU at 210° F.	33.7	34.8	35.9	38.2	41.6	48.1	57.9	208
VI.	105	112	117		135	132	124	115

Flash Point: Cut 1, 340° F.; Cuts 2, 3, 4, 5, 6—395° F. (SSU 39.3); Cuts 3, 4, 5, 6, 7—410° F. (SSU 42.4).

Table II below identifies a plurality of lube oils prepared from blends of the oil fractions presented in Table I. That is, sample 1 of Table II was obtained by blending cuts 2 to 8 of Table I; sample No. 2 of Table II is the same blend as sample 1 but dewaxed at a temperature of minus 35° F.; sample No. 3 of Table II is a blend of cuts 2 to 6 and then dewaxed at minus 35° F.; sample No. 4 is a blend of cuts 3 to 7 of Table II which was dewaxed at minus 35° F.; sample No. 5 is a blend of cuts 3 to 8 of Table II; and sample No. 6 is a blend of cuts 5 to 8 of Table II.

TABLE II.—LUBE OIL BLENDS PREPARED FROM OIL FRACTION OF TABLE I

Sample No.	1	2	3	4	5	6
Dewaxing Temp. ° F.	0	−35	−35	−35	0	0
ASTM Pour, ° F.	0	−10	−25	−20	0	10
Viscosity:						
SSU at 100° F.	325	246	90	113	337	704
SSU at 210° F.	60.8	53.7	39.2	41.7	61.8	89.1
KV at 100° F.	70.24	53.09	18.21	23.65	72.8	151.9
KV at 210° F.	10.43	8.37	3.94	4.71	10.7	17.8
KV at −20° F.	10,000	7,200	1,350	1,800	13,000	36,000
KV at −30° F.	22,000	15,000	2,500	3,300	28,000	75,000
KV at −40° F.	45,000	35,000	5,000	7,500	60,000	180,000
KV at −65° F.	460,000	370,000	47,000	65,000	700,000	2,000,000
Viscosity Index	131	131	130	134	130	124

Presented below in Table III are specifications and characteristics of wide temperature range lube oils which may be prepared by blending and dewaxing the oil fractions of Table I obtained by the aforementioned method.

TABLE III

Viscosity:				
KV at 500° F.			>1.0	1.4
KV at 400° F.		>1.0		2.7
KV at 210° F.	>3.0	(3)	(5.6)	12.1
KV at 100° F.	>11.0	(12.4)	(34)	
KV at −30° F.			<13,000	30,000
KV at −65° F.	<13,000	<21,000		
Pour, ° F. (max.)	−75	−75	−40	−50
Flash, ° F.	400	425	500	505
Fire, ° F.				540
Spontaneous Ignition, ° F.		750	Report	750
Volatility:				
Percent Evaporation at 400° F., 6½ hrs.	<35	<15		
Percent Evaporation at 500° F., 6½ hrs.			<10	6.7

A more detailed description for preparing the aforementioned lubricating oils, suitable for use as vehicles in the improved greases of the present invention, appears in application Serial No. 285,331, filed June 4, 1963 in the names of Michael T. Smilski and Henry R. Ireland, the disclosure of which is incorporated herein by reference.

The above-described lubricating oils are employed in major amounts, with minor amounts of thickening agents to form the improved greases of the present invention. The thickening agent portion of the grease may comprise any of the well-known thickening agents with which the art is familiar. Of particular commercial significance are thickening agents comprised of metal soaps and/or salts of fatty organic acids. Thus, for example, metal soaps of high molecular weight fatty acids may be employed, which may include the alkali metals: sodium, lithium and potassium; and the alkaline earth metals: calcium, barium, strontium and magnesium. The high molecular weight fatty materials may include C_{12} to C_{30}, and preferably C_{16} to C_{22}, saturated or unsaturated grease-making acids such as lauric acid, myristic acid, palmitic acid, stearic acid, hydroxy stearic acid, oleic acid, hydrogenated fish oil acids, linoleic acid, arachidic acid, behenic acid, and various others. Glycerides of the aforementioned acids, vegetable fat, tallow, and others may also be employed as the saponifiable material. Of particular interest in this respect, are the so-called complex soap thickeners with which the art is familiar. Such complex thickening agents include sodium complex soaps prepared by the high temperature saponification of rapeseed oil. If so desired, the amount of complex soap thickener required to thicken the above-described oil vehicle, may be

materially reduced by replacing a portion of the conventional soap thickener with polyolefin resins, without any substantial decrease in structural stability or lowering of the dropping point of the final grease composition.

Various other suitable complex thickening agents may also be employed in the novel grease compositions of the present invention. These may include soap-salt complexes prepared from the metal salts of low molecular weight carboxylic acids having from 1 to 6 carbon atoms per molecule and metal soaps of high molecular weight carboxylic acids having more than 12 carbon atoms per molecule; mixed salt complexes prepared from metal salts of low molecular weight carboxylic acids having from 1 to 6 carbon atoms per molecule and metal salts of intermediate molecular weight carboxylic acids having from 7 to 12 carbon atoms per molecule; soap-salt complexes prepared from a metal salt of acetic acid, metal salts of the aforementioned intermediate molecular weight carboxylic acids and metal soaps of the aforementioned high molecular weight carboxylic acids. A particularly preferred thickening agent comprises ammonium acetate, calcium acetate and calcium caprylate.

The following experimental data will illustrate the improved performance characteristics of the novel greases of the present invention, prepared with the aforementioned hydrocracked oil vehicles, when compared with the identical greases, containing the same grease-forming components, but differing only in the substitution of a conventional mineral oil as the vehicle.

Table IV, below, shows the comparative data obtained with respect to the characteristics of a hydrocracked oil, as previously described, and that of a conventional mineral oil to be used, in each instance, as the oil vehicle, with otherwise identical grease components.

TABLE IV

Properties of Oil	Hydro-cracked Oil	Mineral Oil
Gravity, ° API	36.0	30.0
Flash Point, ° F	450	410
Pour Point, ° F	−5	20
Viscosity KV at 100° F	35.68	44.66
Viscosity KV at 210° F	6.16	6.25
Viscosity SSU at 100° F	171	206.6
Viscosity SSU at 210° F	46.4	46.6
Viscosity Index	129	95
Color, ASTM #D156-53T	<3	2½
4-Ball Wear Test, mm. (167° F.—40 Kg.—1,200 r.p.m.—2 Hrs.) (Federal VVL-791A Method 6514)	0.735	0.92

Employing the hydrocracked oil and the mineral oil described in Table IV, as vehicles in each instance, two separate grease formulations were prepared, in the manner herinafter indicated, resulting in greases having the formulas shown in Table V, below.

TABLE V

	Wt. percent
Sodium 12-hydroxy stearate	2.87
Ammonium acetate	0.90
Calcium acetate·½H_2O	8.03
Calcium caprylate·5% H_2O	5.84
Lime flour	0.42
Antioxidant (2,4 t-butylparacresol)	1.00
Antioxidant (phenyl-a-naphthylamine)	1.00
Oil vehicle	79.94

The respective greases of Table V were prepared in the following manner:

To a grease kettle were added 400 grams (approximately 63%) of the respective oil vehicles, of the formulations disclosed in Table V, together with the sodium 12-hydroxy stearate and ammonium acetate dissolved in equal parts, by weight, of water. The combined materials were thoroughly mixed at room temperature. Thereafter, the calcium acetate·½H_2O and the calcium caprylate·5%H_2O were added, and the combined materials were thoroughly mixed at room temperature. This resulting mixture was

then heated to 420° F., with constant stirring. When the resulting product became thickened and mixing was retarded, the balance of the oil vehicle was then added. Following the aforementioned addition of the balance of the oil vehicle, the resulting mixture was then reheated to 420° F. Thereafter, the lime flour was added, and the mixture was permitted to cool to a temperature of 200° F., with constant stirring. When the mixture had reached a temperature of 200° F., the anti-oxidants, disclosed in Table V, were added, and the resulting mixture was then permitted to cool further to a temperature of 180° F. The resulting product was then passed through a homogenizer, at a setting of 0.001", to produce the respective desired grease compositions.

The greases obtained by the above-described procedure, were then subjected to conventional test procedures, and the results obtained are shown in Table VI.

TABLE VI

ASTM D217-60T Penetration unworked/worked	347/363	322/356
4-Ball Wear Test, mm. Fed. 6514	0.40	0.67
Rolling Stability (2 Hrs. micropenetration Initial/Final) (ASTM D1831-61T)	180/220	176/340
Grease Endurance Life at 350° F. (204 Bearing, 10,000 r.p.m., 5 lbs. Thrust Load), Hrs.	675, 816	148, 176
Avg. (Federal VVL-791A Method 333), Hrs	745	162

The improved results obtained with the novel grease compositions of the present invention containing the above-described hydrocracker oil vehicle, will be apparent from the foregoing data of Table VI. It will be understood, of course, that other grease forming components may be readily substituted for those shown in the foregoing table, in combination with the hydrocracked fluid vehicle as previously described. It will also be understood that other beneficiating materials may also be added to the aforementioned grease compositions, if so desired, as those skilled in the art will readily appreciate. In addition, while preferred embodiments of the novel grease compositions of the present invention and the method for their preparation have been described for purposes of illustration, it will be understood that various modifications and adaptations thereof, which will be obvious to those skilled in the art, may also be made without departing from the spirit and scope of the invention.

I claim:

1. A grease composition consisting essentially of a grease thickener and, as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction to produce a product containing a relatively high boiling lubricating oil fraction, separating said high boiling oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, and thereafter combining portions of said resolved fractions to produce the desired lubricating oil vehicle.

2. A grease composition consisting essentially of a grease thickener and, as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction boiling above about 900° F. to produce a product containing a relatively high boiling lubricating oil fraction, separating said high boiling oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, and thereafter combining portions of said resolved fractions to produce the desired lubricating oil vehicle.

3. A grease composition consisting essentially of a grease thickener and, as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction boiling above about 900° F. to produce a product containing a relatively high boiling lubricating oil fraction having an initial boiling point of at least about 600° F., separating said high boiling oil fraction from said product, resolving said sep-

arated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, and thereafter combining portions of said resolved fractions to produce the desired lubricating oil vehicle.

4. A grease composition consisting essentially of a grease thickener and, as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction to produce a product containing a relatively high boiling lubricating oil fraction, separating said high boiling oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, separately dewaxing said plurality of oil fractions to obtain a plurality of oil fractions having pour points from about −10° F. to about 25° F., and thereafter combining portions of said dewaxed fractions to produce the desired lubrication oil vehicle.

5. A grease composition consisting essentially of a grease thickener and, as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction boiling above about 900° F. to produce a product containing a relatively high boiling lubricating oil fraction, separating said high boiling oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, separately dewaxing said plurality of oil fractions to obtain a plurality of oil fractions having pour points from about −10° F. to about 25° F., and thereafter combining portions of said dewaxed fractions to produce the desired lubricating oil vehicle.

6. A grease composition consisting essentially of a grease thickener and, as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction boiling above about 900° F. to produce a product containing a relatively high boiling lubricating oil fraction having an initial boiling point of at least about 600° F., separating said high boiling oil fraction into a plurality of oil fractions of different boiling ranges, separately dewaxing said plurality of oil fractions at a temperature from about 0° F. to about minus 80° F. to obtain a plurality of oil fractions having pour points from about −10° F. to about 25° F., and thereafter combining portions of said dewaxed fractions to produce the desired lubricating oil vehicle.

7. A grease composition comprising: (A) a lubricating oil vehicle as defined by claim 1, and a gelling agent comprising sodium 12-hydroxy stearate, ammonium acetate, calcium acetate, calcium caprylate and lime flour.

8. A grease composition comprising: (A) as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction to produce a product containing a relatively high boiling lubricating oil fraction, separating said high boiling oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, and thereafter combining portions of said resolved fractions to produce the desired lubricating oil vehicle, and (B) a gelling agent comprising sodium 12-hydroxy stearate, ammonium acetate, calcium acetate, calcium caprylate and lime flour.

9. A grease composition comprising: (A) as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction boiling above about 900° F. to produce a product containing a relatively high boiling lubricating oil fraction, having an initial boiling point of at least about 600° F., separating said high boiling oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, and thereafter combining portions of said resolved fractions to produce the desired lubricating oil vehicle, and (B) a gelling agent comprising sodium 12-hydroxy stearate, ammonium acetate, calcium acetate, calcium caprylate and lime flour.

10. A grease composition comprising: (A) as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction to produce a product containing a relatively high boiling lubricating oil fraction, separating said high boiling lubricating oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, separately dewaxing said plurality of oil fractions to obtain a plurality of oil fractions having pour points from about −10 to about 25° F., and thereafter combining portions of said dewaxed fractions to produce the desired lubricating oil vehicle, and (B) a gelling agent comprising sodium 12-hydroxy stearate, ammonium acetate, calcium acetate, calcium caprylate and lime flour.

11. A grease composition comprising: (A) as a vehicle, a lubricating oil obtained by hydrocracking relatively high boiling resin components of a residual oil fraction boiling above about 900° F. to produce a product containing a relatively high boiling lubricating oil fraction having an initial boiling point of at least about 600° F., separating said high boiling oil fraction from said product, resolving said separated high boiling oil fraction into a plurality of oil fractions of different boiling ranges, separately dewaxing said plurality of oil fractions at a temperature from about 0° F. to about minus 80° F. to obtain a plurality of oil fractions having pour points from about −10° F. to about 25° F., and thereafter combining portions of said dewaxed fractions to produce the desired lubricating oil vehicle, and (B) a gelling agent comprising sodium 12-hydroxy stearate, ammonium acetate, calcium acetate, calcium caprylate and lime flour.

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DANIEL E. WYMAN, *Primary Examiner.*

ABRAHAM RIMENS, *Examiner.*

I. VAUGHN, *Assistant Examiner.*