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MINERAL LUBRICATING OIL CONTAINING WAX ALKYLATED HYDROCARBON AND A COPOLYMER OF ETHYLENE AND VINYL ACETATE

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The present invention relates to novel lubricating oil compositions, and especially to novel aviation lubricating oil compositions, containing dissolved therein pour depressing amounts of a mixture or blend of a wax alkylated aromatic hydrocarbon and a copolymer of ethylene and vinyl acetate.

In the past, when lubricating oil manufacturers desired to produce and market a product which would remain in a fluid state at low temperatures such as those encountered by aircraft based in cold climates, it was necessary to astringently refine fluid distillates used in preparing such lubricating oil fractions. Much effort was expended in dewaxing the mineral oil fraction in order to obtain a low cold test oil, that is, a lubricating oil exhibiting an increase of fluidity at low temperatures. This increase can be attributed to removal of the long needle-shaped wax crystals, normally present in the mineral oil which interlocked and, thereby, entrapped oil. In later developments oils containing appreciable amounts of wax were found to be somewhat satisfactory under low temperature conditions where materials were added which tended to inhibit the formation of the long needle-shaped crystals and insure free flow at low temperatures. As employed herein, the temperature at which an oil loses its properties of free flow is referred to as its "pour point."

It is an object of the instant invention, therefore, to add a noval blend of additives to either wax free lubricating oils or to lubricating oils containing wax in such an amount as to lower their pour point. It is a particular object of this invention to markedly lower the dilute pour point exhibited by aviation lubricating oils.

Heretofore, a wide variety of compounds has been found suitable as pour point depressants for lubricating oils. One type of pour depressant can be made by chlorinating paraffin wax and condensing the chlorinated paraffin wax with an aromatic hydrocarbon such as benzene, naphthalene, or anthracene in the presence of a Friedel-Crafts type catalyst such as aluminum chloride. U.S. Patent Nos. 1,815,022, 2,087,682 and 2,174,246 describe in detail procedures for making the chlorinated-wax-aromatic type of pour point depressants and are incorporated herein by reference. Another type of pour point depressants for use in either lubricating oils or in gasoline can be made by copolymerizing N-vnyl pyrrolidones and their alkyl derivatives with alkyl esters of acrylic acid or of methacrylic acid. The preparation of these pour point depressants is disclosed in detail in U.S. Patent 3,058,818 which is incorporated herein by reference.

It was found, however, that these conventional pour point depressants, did not effectively lower the pour points

of aviation oils to a sufficient extent to permit such oils to be acceptable for engines employed in aircraft based in extremely cold climates. Similarly, it was found that a combination of wax alkylated aromatic pour point depressants with the heretofore mentioned ester type pour point depressants likewise failed to achieve a sufficient lowering of the pour point (particularly with reference to the dilute pour point requirements) to produce a blend of these two materials which was consistently acceptable for use in aviation oils. This failure resulted in the test for pour point properties of the oil, as well as in the test for the dilute pour point properties of the oil; both tests presently employed to determine the suitability of aviation oils.

In accordance with the present invention, it has been discovered that a mineral lubricating oil composition comprising a major amount of a hydrocarbon mineral lubricating oil with a pour depressing amount of a mixture of a wax alkylated aromatic hydrocarbon and a copolymer of ethylene and vinyl acetate find utility as an aviation lubricating oil which meets specifications both as to pour point and dilute pour point. This is indeed surprising for, as will be illustrated by comparative data, neither of the materials of the mixture, when used alone, accomplishes the utility of the ethylene vinyl acetate copolymer, i.e., each material shows practically no pour point depressant activities when added to lubricating oil. It is noteworthy that U.S. Patent 3,087,894 teaches that the low molecular weight copolymers of ethylene and vinyl acetate have no effect upon the pour point of lubricating oil and emphasizes the difference in structure between the wax associated with lube oils and the wax associated with middle distillates. The copolymer molecular weights defined in such patent range from about 1,000 to about 3,000. In the instant case, the molecular weights of ethylene-vinyl acetate copolymers are higher but such higher molecular weights of the ethylene-vinyl acetate copolymers have also heretofore been deemed essentially inactive as a pour point depressant. It was, therefore, surprising to discover that the use of a conventional pour point depressant, i.e., wax alkylated naphthalene, which by itself failed to meet specifications as to dilute pour point, could be combined and yield a synergistically suitable aviation lubricating oil when combined with an ethylene-vinyl acetate copolymer which exhibited no effect per se as a pour point depressant in aviation lubricating oil.

The ethylene-vinyl acetate copolymers are obtained by heating a mixture of ethylene and vinyl acetate at a temperature ranging between about 100° and about 400° C. with or without the presence of a solvent such as benzene or heptane under super-atmospheric pressures of between about 100 and about 2,000 atmospheres. Generally, the reaction is expedited if an oxidation catalyst such as a peroxide or hydroperoxide, for example, benzoyl peroxide or tertiary butyl hydroperoxide, is also present. After reaction the resulting copolymer is separated from the unreacted monomers by flashing off the latter.

The mole ratio of ethylene to vinyl acetate may be varied to affect the melt index, inherent viscosity, as well

as the viscosity average molecular weight of the resultant copolymer. The melt index may range from about 1 to about 1,000 but it is preferred to employ an ethylene-vinyl acetate copolymer having a melt index ranging between about 2 and about 500. These melt indices correspond to average molecular weights of between about 1500 and 500,000, preferably between about 2000 and about 300,000, measured according to the method of K. Rast (Ber. 55, 1051, 3727 (1922)). For best results, an ethylene to vinyl acetate mole ratio in the copolymer of between about 0.25:1 and about 20:1 is used with the resultant copolymer having a melt index of somewhere between 2.5 and 475. A particularly preferred copolymer is one containing between 5 and 30 wt. percent of vinyl acetate and one preferably having a melt index ranging between 10 and 200. These copolymers are oil soluble and may be preblended as a concentrate into a lubricating oil fraction which serves as a vehicle. For convenience, this concentrate may contain from 40–75 wt. percent of the blend of pour point depressants. The relative ratios of the depressants may vary over a considerable range but is generally between about 0.1 and 8 parts of wax alkylated aromatic hydrocarbon per part of ethylene-vinyl acetate copolymer. Highly effective results have been obtained where between 2 and 3 parts of wax alkylated aromatic hydrocarbon are used per part of ethylene-vinyl acetate copolymer. The relative amount of additives employed in the lubricating oil composition ranges between about 0.01 and about 5.0 wt. percent of the wax alkylated aromatic hydrocarbon and between about 0.02 and about 10 wt. percent of the vinyl acetate-ethylene copolymer, both percentages being based on the total weight of said lubricating oil composition. Specifically it is preferred to employ from about 0.05 up to about 0.5 wt. percent on the same basis of each of the two types of additives.

To be acceptable for commercial and military aircraft use, the aviation lubricating oils must meet the dilute pour point test which is denoted in the United States as U.S. Military Specification L–6082C and in Canada as Canadian Military Specification 3GP320. This test requires that the lubricating oil must have a dilute pour point of at least —50° F. for 3GP320 and a dilute pour point of at least —65° F. for L–6082C under a standard set of conditions as outlined in those specifications. Efforts have been made to fulfill this requirement through the use of combinations of known lubricating oil pour point depressants, for example, an aviation lubricating oil comprising 44.4 wt. percent of a Mid-Continent lubricating oil stock having the specifications: +20° pour point, a viscosity index of 109.7, an API gravity of 30.5°, a viscosity of 59 SUS at 210° F. and 400 SUS at 100° F., and a flash point of 490° F. Cleveland open cup method (COC) admixed with 52.7% of a Mid-Continent lubricating oil fraction having the specifications: +15° F. pour point, a viscosity index of 100.5, an API gravity of 26.9°, a viscosity of 146 SUS at 210° F. and 22,224 SUS at 100° F., and a flash point of 580° F. COC. As in commercial operation, this was admixed with 2.9% of an N-vinyl pyrrolidone type

preparation disclosed in U.S. Patent 3,058,818. To this base oil, referred to as (A), which had a pour point of "0° F." and a dilute pour point of —40° F. when measured in isooctane (Canadian military specification), was added, in separate aliquots, (B) wax alkylated naphthalene, (C) a prior pour depressant prepared according to specification of U.S. Patent 2,710,842, (D) a mixture of 75 wt. percent wax alkylated naphthalene and 25 wt. percent of a mixture of vinyl acetate with the ester prepared from Lorol alcohol and fumaric acid. Additionally, an aliquot was used containing a measured amount of an ethylene-vinyl acetate copolymer, (E) containing about 27% vinyl acetate and having a molecular weight by the aforementioned method of about 2,000. The following results were obtained:

TABLE I

Base Oil and Pour Depressant	(A)	(A)+(B)		(A)+(C)		(A)+(D)		(A)+(E)	
Concentration, Percent	0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
Pour Point (ASTM D97-57)	0	—10	—15	—10	—15	—15	—15	0	0
Dilute pour point (Canadian Method)	—40	—45	—40	—45	*—50	—40	—45	—40	—40

*Could not be duplicated.

It is readily apparent from the above pour point and dilute pour point data that a combination of (A) with any of the other four materials tested as pour point depressants did not produce a dilute pour point which would meet specifications of —50° F. required by the Canadian military specification method. The base oil employed was a commercially available aviation lubricating oil.

The following examples are presented as illustrative of the invention herein described but they are not intended to be limiting in any sense:

Example I

An aviation lubricating oil base stock comprised the following components.

(a) 61 wt. percent Mid-Continent "bright stock" of the following components.

Pour point, ° F.	+20
Viscosity index	103
API gravity	26.50
Viscosity, SUS @ 100° F.	1,192
Viscosity, SUS @ 210° F.	155
Flash point (COC), ° F.	560

(b) 39 wt. percent Mid-Continent lubricating oil fraction (Barosa 56) of the following specifications:

Pour point, ° F.	+20
Viscosity index	109.7
API gravity	30.5
Viscosity, SUS @ 100° F.	400
Viscosity, SUS @ 210° F.	59
Flash point (COC), ° F.	490

This blend of lubricating oils had a viscosity index of 105.6 and had an ASTM pour point of +20° F. To this base stock was added varying amounts of pour point depressants under comparative conditions as shown in the folowing Table II. Three pour point determinations were made on each blend, i.e., the standard ASTM pour point determination, the dilute pour point determination made in iso-octane in accordance with the aforementioned Canadian military specification and the dilute pour point determination in a mixture of heptane and xylol in ac-

cordance with the aforementioned U.S. military aviation specification. The data obtained are as follows:

TABLE II

Run No.	Percent by Wt. Additive in Base Stock	Pour Point, ° F. (ASTM D97-57)	Dilute Pour Point, ° F. in—	
			Isooctane [1]	Heptane-Xylol [2]
1	None	+20	−15	−20
2	0.1% E/VA [3]	+20	−35	−35
3	0.2% E/VA	+15	−35	−35
4	0.3% E/VA	+15	−40	−35
5	0.1% E/VB [4]	+15	−35	−40
6	0.3% E/VB	+15	−40	−35
7	0.1% E/VC—Elvax 460 [5]	+15	−35	−35
8	0.1% E/VD [6]	+15	−5	−15
9	0.3% wax alkylated naphthalene	+15	−35	−35
10	0.1% E/VA—0.2% wax alkylated naphthalene	+15	−65	[7] −65
11	0.1% E/VA—0.3% wax alkylated naphthalene	+15	−65	[7] −65
12	0.1% E/VB—0.3% wax alkylated naphthalene	+10	−65	[7] −65
13	0.1% E/VC—0.3% wax alkylated naphthalene	+10	−55	−60
14	0.1% E/VD—0.3% wax alkylated naphthalene	+15	−25	−35
15	0.3% E/VA—0.3% wax alkylated naphthalene	+10	−65	[8] −65
16	0.3% E/VB—0.3% wax alkylated naphthalene	+10	−65	[8] −65
	Specification		[9] −65	[9] −65

[1] Canadian Military Specification Solvent.
[2] United States Military Specification Solvent.
[3] Ethylene-vinyl acetate copolymer, 27–29% vinyl acetate, melt index 125–175 (ASTM D1238).
[4] Ethylene-vinyl acetate copolymer, 27–29% vinyl acetate, melt index 2.4–3.4.
[5] Ethylene-vinyl acetate copolymer, 17–19% vinyl acetate, melt index 125–175.
[6] Ethylene-vinyl acetate copolymer, 27–29% vinyl acetate, melt index over 1000.
[7] −65 or below.
[8] −65 or lower.
[9] −65 max.

It should be noted that Run Nos. 1 through 9 did not achieve the dilute pour point specification of at least −50° F. At the same time Run Nos. 10 through 13 and 15 and 16 did achieve the desired dilute pour point specifications.

Example II

An additional series of runs were carried out using various aviation base oil blends in which all base blends contained 2.9 wt. percent of an N-vinyl pyrrolidone type pour depressant as disclosed in U.S. Patent 3,058,818 and 0.32% of a bisphenol anti-oxidant. All runs also contained 0.3 wt. percent of wax alkylated naphthalene. The data obtained and an explanation of the base oils employed are as follows:

TABLE III

Run No.	17	18	19	20
Barosa 56 of Example I	52.7	52.7		
325 Neutral Oil [1]			43.7	43.7
Bright stock [2]	44.4	44.4		
Bright stock of Example I			53.4	53.4
N-vinyl pyrrolidone type polymer	2.9	2.9	2.9	2.9
Bisphenol anti-oxidant	0.32	0.32	0.32	0.32
Wax alkylated naphthalene	0.3	0.3	0.3	0.3
E/VA		0.1		0.1
Pour point, ° F	−10	−10	−10	−10
Dilute pour point, ° F. Heptane/Xylene (2)	−40	−50	−35	−55
Iso-octane (1)	−40	−50	−35	−55

[1] Solvent dewaxed, solvent extracted, neutral Mid-Continent oil:
Pour point, ° F +15
Viscosity index 100
API gravity 29.0
Viscosity, SUS @ 100° F 325–340
Viscosity, SUS @ 210° F 50
Flash point (COC), ° F 450
[2] Mid-Continent bright stock of the following inspection:
Pour point, ° F +15
Viscosity index 100.5
API gravity 26.9
Viscosity, SUS @ 100° F 2,224
Viscosity, SUS @ 210° F 146
Flash point (COC), ° F 580

Run Nos. 17 and 19 contained no ethylene-vinyl acetate copolymer. Run Nos. 18 and 20 contained .1 of 1% of ethylene-vinyl acetate copolymer which was the same copolymer as employed in the blends shown in Table II and corresponds to the copolymer explained in footnote 3 of that table.

These data amply illustrate that the 36P320 dilute pour point specifications are met in the case where ethylene-vinyl acetate copolymer was used in the amount of .1 of 1%; Run No. 18 showing a dilute pour point of −50° F. and Run No. 20 showing a dilute pour point of −55° F. The reference numbers which are not explained in the footnotes of Table III are the same reference numbers as shown in Table II and as explained therein.

Additional runs were effected in order to illustrate the operability and effectiveness of various ethylene-vinyl acetate copolymers when employed in the depressant compositions of this invention. The data illustrate vinyl acetate (VA) contents of from 6% to 27% and copolymer molecular weights in the range of from 2000 to 6500. Particular attention should be directed to the advantageous results accruing from use of an ethylene-vinyl acetate copolymer of 2000 molecular weight and a VA content of 6%.

TABLE IV

[Base oil same as for Run No. 18 on Table III]

Run No.	18 [1]	18 [2]	18 [3]	18 [4]
E/VA, percent	0.1	0.1	0.1	0.1
Pour	−10	−10	−15	−10
Dilute Pour in Isooctane	−50	−65	−50	−50
Dilute Pour in Heptane/Xylol	−65	[5] −65	−50	−50

[1] Copolymer M.W.=3,500, Percent VA=18 (Allied Chemical, AC-400).
[2] Copolymer M.W.=2,000, Percent VA=6% (Allied Chemical, G-201).
[3] Copolymer M.W.=6,500, Percent VA=27.
[4] Copolymer M.W.=4,700, Percent VA=20.8.
[5] −65 or lower.

It is not intended that this invention be limited to the specific examples presented by way of illustration. The scope of the invention is limited only by the appended claims.

What is claimed is:

1. An aviation lubricating oil composition having a dilute pour point of −50° F. or lower, as measured in isooctane, comprising a major amount of a mineral hydrocarbon aviation oil; in the range of about 0.1 to about 5 wt. percent of a wax alkylated aromatic hydrocarbon pour point depressant; and in the range of about 0.02 to about 10 wt. percent of a copolymer of ethylene and vinyl acetate pour point depressant, said copolymer having a melt index within the range of about 2 to about 500, an average molecular weight within the range of about 1500 and about 500,000 and containing about 0.25 to about 20 moles of ethylene per mole of vinyl acetate; and wherein said wax alkylated hydrocarbon and said copolymer synergistically reduce said dilute pour point of said oil.

2. A composition according to claim 1, wherein said

aromatic hydrocarbon is naphthalene, wherein the amount of vinyl acetate in said copolymer is between 5 to 30 wt. percent, and wherein the amount of said wax alkylated hydrocarbon is about 2 to 3 times the amount of said copolymer.

3. A composition according to claim 1, wherein said oil contains about 0.3 wt. percent of wax alkylated naphthalene and about 0.1 wt. percent of said copolymers.

References Cited

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