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DETERGENT MULTIGRADE LUBRICANT

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This invention relates to lubricating oils and in particular to multigraded lubricating compositions characterized by improved detergent-dispersant properties.

The SAE system of classifying motor oils is based on the viscosity of the oil at both 0° F. and 210° F. for the winter grades and at 210° F. for the other grades. If the viscosity index is sufficiently high it is thus possible for one oil to meet the viscosity requirements of more than one SAE grade. Such oils are known as multigraded lubricating oils and although of relatively recent origin, these oils are becoming widely used in many internal combustion engines where severe operating conditions are encountered. Generally multigraded lubricating oils contain a large or major amount of a mineral oil together with minor amounts of various oil-soluble additive agents such as pour depressors, viscosity index improvers, detergents, sulfurized fatty oils and the like which are designed to improve the characteristics of the oil in one or more respects. Unfortunately, however, many of these oils which contain a detergent additive fail to provide satisfactory performance even though single graded oils containing the same detergent in an equal amount will give satisfactory results. For example, two oils, an SAE 10W and an SAE 10W–30, were blended to the same detergent level with basic barium petroleum mahogany sulfonate and tested in a Caterpillar single cylinder engine by the AXS–1551 and 2–104B test procedures. In these tests the detergency characteristics of the oil are rated with respect to the carbonaceous deposits developed in the ring grooves and ring lands. From the data obtained (see Example I below) it was found that the multigraded 10W–30 oil failed to give satisfactory detergent performance, as indicated by a top groove filling of 43.8 percent, whereas the single graded 10W oil gave a top groove filling of only 8.5 percent. Even when the multigraded oil was blended to a higher detergent level, undesirable deposits occurred in the fourth ring groove which still indicated unsatisfactory performance. Consequently, a need exists for multigraded oils which display satisfactory detergency characteristics as evidenced by low carbonaceous deposit-forming tendencies.

In accordance with this invention, I have discovered that the addition of oil-soluble carbonated basic barium petroleum sulfonates to multigrade mineral lubricating oil compositions imparts highly desirable properties to the composition. It has been found that in multigraded lubricating oils which employ a methacrylate type additive agent, improved detergent-dispersant properties can be obtained by use of an oil-soluble basic barium petroleum sulfonate which has been treated with carbon dioxide. As compared to the basic barium sulfonates, the carbonated sulfonate not only provides a multigraded lubricating oil having a more satisfactory engine performance, but also provides a means whereby appreciable savings in cost are obtained since the amount of detergent necessary to effectively minimize the formation of harmful deposits can be reduced by more than thirty percent. Although the reasons for improved detergent characteristics are not known, it is believed that in combination with multigraded lubricating oil compositions which contain polymeric methacrylate materials, the carbonated sulfonate avoids interaction between these

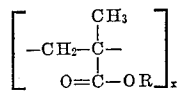
materials and the sulfonate and thus permits the detergent to control carbonaceous deposits more effectively.

The lubricating compositions of the invention are prepared by compounding a small amount of an oil-soluble carbonated basic barium mahogany sulfonate in a multigraded mineral lubricating oil composition which contains from about 1.0 to 3 percent of a methacrylate polymer type additive agent, preferably at least about 2.0 percent, based on the lubricating oil of the composition. The hydrocarbon lubricating base oils which are used in making the compositions are derived from paraffinic, naphthenic, or mixed base mineral oil crudes, and preferably encompass a viscosity range of from about 40 to 70 SUS at 210° F. Suitable illustrative hydrocarbon oils include, for example, solvent refined Pennsylvania and Mid-Continent distillate oils, as well as Western or Gulf Coast distillate oils and bright stocks from these various crude oils. The hydrocarbon oils which are preferred are characterized by a high viscosity index of at least 85, preferably at least about 90. In this invention these oils are compounded with the methacrylate additive and the resulting compositions meet the viscosity requirements of at least three SAE grades, generally a minimum viscosity index of about 110. For example, typical viscosities of multigraded hydrocarbon oil compositions are as follows:

SAE Grade	Viscosities			Minimum Viscosity Index
	0° F.	(Extp.) 100° F.	210° F.	
5W–20	4,000	141	45	140.0
10W–30	12,000	294	58	130.7
20W–40	48,000	545	70	110.2
10W–40	12,000	380	70	138.8

The oil-soluble carbonated basic barium petroleum mahogany sulfonates which are used in this invention are the basic salts or soaps of oil-soluble petroleum sulfonic acids, referred to as mahogany acids, which are obtained by the sulfuric acid, oleum or sulfur trioxide treatment of petroleum oils boiling primarily within the range of about 600 to 1000° F. The basic sulfonates can be prepared by neutralizing the mahogany acids with an excess of a basic barium compound, such as barium hydroxide, so as to obtain a product which contains an amount of barium in excess of that theoretically required to neutralize the acid or replace the acidic hydrogens. Generally, the amount of barium neutralizing agent employed in obtaining the basic sulfonates is at least 1.5 times the theoretical amount required for neutralization. The basic barium sulfonate is conveniently employed as a 10 to 50 percent concentrate, preferably a 10 to 30 percent concentrate, in the mineral oil from which it is derived and can be carbonated by any convenient method. As an example, a concentrate of basic barium sulfonate in mineral oil can be contacted with carbon dioxide gas until the strong basicity of the sulfonate to phenophthalein is destroyed and a final pH of about 7 to 8.5, preferably about 8, is obtained. The carbonation treatment may be carried out by introducing the basic barium sulfonate to the top of a packed column and then feeding carbon dioxide gas through the bottom of the column. The carbonated basic barium sulfonate is then recovered and vacuum dried to obtain the final product. Generally, in the practice of this invention it is preferred that the carbonated basic barium petroleum mahogany sulfonate be present in the multigraded lubricating oil in an amount sufficient to provide a barium content of about 0.5 to 1.5 percent, and preferably in an amount ranging from about 0.7 to 1.3 percent by weight, based on the base oil.

The methacrylate type additive agents used in the lubricating composition of this invention are the lubricating oil-compatible methacrylate ester copolymers which have the formula



in which R is a mixture of alkyl groups containing from 4 to 20 carbon atoms and x is the number of molecules condensed together to form a high molecular weight polymer of about 5,000 to 20,000 molecular weight. These materials include a series of commercially available polymers known as "Acryloids," some of which are described in U.S. Patent No. 2,710,842, issued June 14, 1955. The polymers function mainly as a viscosity index improver and secondarily as pour point depressors. The methacrylate polymers are generally employed as a concentrate in solvent refined neutral oils, usually a 40 weight percent concentration, and a typical polymer Acryloid 710 has the following physical properties:

Sp. gr., 60° F./60° F.	0.096
Lbs./gal.	7.54
Flash point, C.O.C., ° F.[1]	400
Pour point, ASTM, ° F.[2]	25
Viscosity, cs./100° F.	9,400
Viscosity, SUS/100° F.	43,000
Viscosity, cs./210° F.	800
Color, ASTM	3
Neut. No.	0.2

[1] When diluted three parts of a 400° F. flash mineral oil to decrease the viscosity.
[2] Viscosity pour point.

In addition to compounding the multigraded base oil with the carbonated basic barium mahogany sulfonate and methacrylate materials, other additive agents such as extreme pressure agents, anti-oxidants, anti-foam additives, and the like, can be employed to improve the oil in one or more respects. For example, in order to impart extreme pressure properties a material such as sulfurized sperm oil can be used in amounts ranging from about 1 to 3 weight percent on the base oil. This material is well known and may be prepared by sulfurizing either sperm oil, or a mixture of mainly sperm oil and lanolin, with about 8 to 15 percent of sulfur at 350 to 400° F. for about one to three hours. The resulting sulfurized product contains about 7 to 15 percent of combined sulfur in a form which renders the product non-corrosive in the copper strip corrosion test.

Among the anti-oxidant type additive agents which can be used to improve the multigraded compositions of this invention are the nickel and zinc dithiophosphates which are obtained from a wide variety of diester dithiophosphoric acids conventionally prepared by reacting a sulfide of phosphorus, such as phosphorus pentasulfide, with an alcohol, phenol or mercaptan. The organic groups in the acid esters may be aryl, alkyl, aralkyl or cycloalkyl groups which contain from about 4 to 20 carbon atoms, preferably about 6 to 14 carbon atoms, and may be further substituted if desired. A suitable zinc dithiophosphate which may be employed is the zinc salt obtained from a mixed dithiophosphate prepared by reacting a technical mixture of C_7 secondary and C_8 primary alcohols, mainly the former, with phosphorus pentasulfide. Nickel dithiophosphates which can be employed may be prepared from a di-2-ethylhexyl dithiophosphate obtained by reacting a technical mixture of 2-ethylhexanol with phosphorus pentasulfide. The zinc and nickel dithiophosphates are used in the lubricating compositions in a minor amount sufficient to inhibit oxidation and bearing corrosion and in most instances the amount employed provides about 0.03 to 0.2 percent by weight of phosphorus to the multigraded oil in which it is incorporated.

Anti-foam agents are particularly desirable in the multigraded lubricating composition for inhibiting foam and gas entrainment and for this purpose silicon oxide condensation polymer products such as polymers of dimethyl silicone, methyl phenyl silicone, ethyl butyl silicone, etc. can be employed. These materials and their method of preparation are well known to the art and are described in U.S. Patent No. 2,662,055.

The silicon oxide anti-foam agents are conveniently handled as a 10 percent concentrate in a hydrocarbon solvent such as kerosene and in the specific examples shown below, a concentrate was prepared by dissolving 10 grams of dimethyl silicone polymer in a sufficient amount of kerosene to make up a total volume of 100 cc. The silicone polymer concentrate is preferably employed in the multigraded hydrocarbon base oil in a proportion of about 0.001 to 0.05 percent by weight.

The lubricating compositions of this invention are illustrated by the following examples which are not to be considered as limiting.

Example I

Three oils, an SAE 10W, SAE 30 and SAE 10W–30, were prepared which had the following composition:

Base Oils, Volume Percent	Vis. SUS at 100° F.	SAE 10W	SAE 30	SAE 10W–30
Solvent Refined Mid-Continent Neutral	79	51	--------	13
Do	160	49	--------	87
Do	615	--------	100	--------
Additives, Wt. Percent on Base Oil:				
Basic Barium Mahogany Sulfonate [1]	----------	27	23	27
Zinc Dialkyldithiophosphate [2]	----------	1.7	1.7	1.7
Methacrylate Polymer [3]	----------	1.7	0.9	5.5
Sulfurized Sperm Oil (11.5% S)	----------	--------	1.25	--------
Dimethyl Silicone Polymer [4]	----------	0.005	0.005	0.005
Inspection Tests:				
Viscosity, SUS—				
at 100° F	----------	166	529	297
at 210° F	----------	46.1	65.9	60.6
Percent Barium	----------	0.93	0.79	0.93

[1] A 14% concentrate in mineral oil solution which analyzes 3.5% barium (about twice that calculated to give a neutral sulfonate).
[2] Prepared from four moles of mixed C_6 and C_7 alcohols with one mol of P_2S_5 at 160 to 170° F. Product analyzed 10.5% sulfur and 5.5% phosphorus as an approximate 50% concentration in lube oil.
[3] Acryloid 763; a 40% concentrate in mineral oil of methacrylate ester polymer in which the ester groups are derived from a mixture of alcohols n the C_6 to C_{18} range.
[4] Kinematic viscosity of 100 centistokes at 25° C.

The above oils were tested in a Caterpillar single cylinder engine by the AXS–1551 procedure except that the fuel contained one percent sulfur. In this test, the rings, grooves and lands are rated for deposits. A maximum of 25 percent filling of the top groove with deposits is allowable under the defunct but more rigorous Army 2–104B (Supplement I) specifications. The following results show that the multigraded SAE 10W–30 failed to give satisfactory detergent-dispersant performance even though the same amount of detergent gave a satisfactory rating in the single graded oils.

	SAE 10W	SAE 30	SAE 10W-30
Percent Top Groove Filling	8.5	13	43.8.
2nd Groove—Percent Area Covered by Deposits.	Trace Lacquer.	5-Soot	37-Thin Carbon.
Balance of Ring Belt Area	Essentially Clean.	Essentially Clean.	Essentially Clean.

Example II

Two 10W–30 multigraded oils, designated A and B, were formulated in which higher amounts of basic bari-

um sulfonate detergent were employed. The blends had the following composition:

Base Oils, Volume Percent	Blend A	Blend B
Solvent Refined Mid-Continent Neutral:		
160 SUS at 100° F	78	65
200 SUS at 100° F	22	35
Additives, Wt. Percent on Base Oil:		
Basic Barium Mahogany Sulfonate*	40	65
Zinc Dialkyldithiophosphate*	2	2
Methacrylate Polymer [1]	6.2	6.2
Sulfurized Sperm Oil (11.5% S)	1.25	1.25
Dimethyl Silicone Polymer*	0.001	0.001
Percent Barium	1.40	2.32

*See Example I.

[1] Acryloid 618, 40% concentration of polymethacrylate polymer in oil solution; ASTM Pour Point, ° F. of +40; Vis. SUS at 100° F. of 106,000, the ester groups are derived from a mixture of alcohols in the C_8 to C_{18} range.

As shown below, results of the Caterpillar engine tests carried out on blends A and B indicate that the detergent level corresponding to 1.40 percent barium is inadequate for satisfactory performance in this oil. The 2.32 percent barium level, although more than adequate for the top groove, is still unsatisfactory because of undesirable deposits in the fourth groove. In these oils it was estimated that a minimum barium content of 1.9 percent would be necessary to provide satisfactory performance. In different base oils, however, a barium level of 1.75 percent was found satisfactory.

	Blend A	Blend B
Percent Top Groove Filling	46 [1]	4.5.
2nd Groove—Percent Area Covered by Deposits.	1-Hard Carbon.	Clean.
4th Groove—Percent Area Covered by Deposits.	Clean	40-Lacquer.
Balance of Ring Belt Area	Essentially Clean.	Essentially Clean.

[1] Test stopped at 274 hours; regular test is of 480 hours' duration.

Example III

A multigraded SAE 10W–30 hydrocarbon oil composition prepared in accordance with this invention and identified as blend C had the following composition.

Base Oils, Volume Percent	Blend C
Solvent Refined Mid-Continent Neutral:	
160 SUS at 100° F	76
200 SUS at 100° F	24
Viscosity Index	95
Additives, Wt. Percent on Base Oil:	
Carbonated Basic Barium Mahogany Sulfonate [1]	37
Zinc Dialkyldithiophosphate*	2
Methacrylate Polymer*	6.2
Sulfurized Sperm Oil (11.5% S)	1.25
Dimethyl Silicone Polymer*	.001
Inspection Tests:	
Viscosity SUS at 100° F	339.6
Viscosity SUS at 210° F	68.7
Viscosity Index	142.2
Percent Barium	1.3

*As in Example II.

[1] Basic barium petroleum mahogany sulfonate treated with moist carbon dioxide until the initial pH is reduced to about 7 to 8. Employed as a 14% concentrate in the mineral oil from which it was derived which analyzed 3.5% barium.

The above composition was tested in the Caterpillar single cylinder engine test and the following results were obtained:

Blend C:

Percent top groove filling 16
Balance of ring belt ..... Clean

As seen from these data, the carbonated basic barium sulfonate provided satisfactory detergent performance when blended to a barium level of 1.3 percent. As compared to Example II wherein a minimum estimated barium content of 1.9 percent was needed for a non-carbonated basic barium sulfonate, the amount of detergent was reduced by more than 30 percent when added to essentially the same base oil.

Example IV

In this example two multigraded SAE 10W–30 oil blends designated D and E were prepared as follows:

Base Oils, Volume Percent	D	E
Solvent Refined Mid-Continent Neutral:		
160 SUS at 100° F	50	50
200 SUS at 100° F	50	50
Viscosity Index	95	95
Additives, Wt. Percent on Base Oil:		
Non-carbonated Basic Barium Sulfonate [1]	15.4	-------
Carbonated Basic Barium Sulfonate [2]	-------	15.4
Zinc Dialkyldithiophosphate*	1.27	1.27
Nickel di-2-ethylhexyl dithiophosphate [3]	0.68	0.68
Methacrylate Polymer*	5.3	5.3
Sulfurized Sperm Oil (12% S)	1.25	1.25
Dimethyl Silicone Polymer*	0.005	0.005
Inspection Tests:		
Viscosity, SUS at 100° F	358	325
Viscosity, SUS at 210° F	67.0	66.0
Percent Barium	1.22	1.21
Viscosity Index	138	142.5

*As in Example III.

[1] Basic barium mahogany sulfonate prepared from a dewaxed Sweet West Texas gas oil. The sulfonate analyzed 7.95% barium and had a base number to pH 4 of 28.6.

[2] A portion of basic barium sulfonate (1) was treated with moist carbon dioxide until the initial pH of about 14 dropped to 7.1. It analyzed 7.83% barium and had a base number to pH 4 of 27.3.

[3] Prepared by reacting about 345 grams of di-2-ethylhexyl dithiophosphoric acid with 60 grams of nickel carbonate in the presence of toluene and water at a temperature of about 150 to 200° F. Final product analyzed about 7.24% phosphorus and was blended to 0.05% phosphorus level.

The following Caterpillar engine results were obtained on blends D and E. The fuel contained one percent sulfur.

	D	E
Percent Top Groove Filling	53.7 [1]	23.
1st Land, Percent Area Covered by Deposit	20%-Lacquer Clean.	Clean.
Balance of Ring Belt	Clean	Clean.

[1] Test was halted at 316 hours.

As readily seen, the above results show that at substantially the same barium level in the multigraded hydrocarbon oils, the carbonated basic barium sulfonate provided more satisfactory engine performance.

It is claimed:

1. A lubricating composition consisting essentially of a major amount of a mineral oil of lubricating viscosity and having incorporated therein from about 1 to 3 percent by weight of a methacrylate ester polymer in which the ester radical contains 4 to 20 carbon atoms to provide a lubricating composition whose viscosity characteristics satisfy at least three SAE grades and a small amount of an oil-soluble carbonated basic barium petroleum mahogany sulfonate, said sulfonate being sufficient to provide a barium content of about 0.5 to 1.5 percent by weight.

2. The lubricating composition of claim 1 wherein said barium content is from about 0.7 to 1.3 percent by weight.

3. The lubricating composition of claim 1 which contains a small amount of zinc dithiophosphate diester in which the organic groups contain from about 4 to 20 carbon atoms sufficient to provide a phosphorus level of from about 0.03 to 0.2 percent by weight.

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7

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8

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