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LUBRICANT CONTAINING MIXTURE OF LOW AND HIGH MOLECULAR WEIGHT SULFONATES

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ABSTRACT OF THE DISCLOSURE

Anti-rust and cleanliness properties of lubricating oils are improved by the addition of a blend of high and low molecular weight highly basic alkaline-earth metal petroleum sulfonates.

This invention relates to lubricating compositions, and particularly to lubricating compositions containing a highly basic alkaline earth metal sulfonate additive which imparts good anti-rust and cleanliness properties thereto.

It is known that basic calcium sulfonates are useful components of lubricants for internal combustion engines. These sulfonates contain excess base which imparts "alkaline reserve" to the lubricant, the alkaline reserve neutralizes sulfur and acids during application of the lubricant. Sulfonates of this type which have a molecular weight of about 470 are good rust inhibitors, but they promote low temperature sludging characteristics of the lubricant. The higher molecular weight sulfonates of this type do not promote low temperature sludging, but the anti-rust activity thereof is not acceptable.

It has now been found in accordance with the present invention that an internal combustion engine lubricant containing an oil-soluble additive consisting essentially of a blend or mixture of (1) low molecular weight and (2) high molecular weight, highly basic, alkaline earth metal sulfonates possesses good anti-rust activity without promoting undesirable characteristics, such as the expected low temperature sludging characteristics.

The sulfonates may be either synthetic or petroleum sulfonates. The terms "petroleum sulfonate" or "petroleum sulfonic acids" as used in this specification are intended to cover all sulfonates or sulfonic acids which are derived directly from petroleum products, such as lubricating oils. The term "synthetic sulfonate" is intended to include all sulfonates which are not petroleum sulfonates. By "basic sulfonate" is meant that the end product contains excess base and has a basicity of at least 20% and up to 1000% or more. Basicity of the subject sulfonates is usually defined as the excess of metal in the sulfonate over that quantity of metal which would be present in the normal (non-basic) sulfonate. The excess base appears to be present in the sulfonate in the form of the original base used to neutralize the acid. Thus, if the content of metal in a particular sulfonate mixture is (a) percent by weight, and if the content of metal the mixture would have if it were present only as the normal

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sulfonate is (b) percent by weight, then the basicity of the mixture is

$$\frac{(a)-(b)}{(b)}\times 100\%$$

it can also be expressed as percent basicity=moles $[CaCO_3+Ca(OH)_2]\times 100$/moles $Ca(SO_3R)_2$.

The low molecular weight sulfonate component of the additive has an average equivalent weight of from about 450 to 550, and may be a petroleum sulfonate prepared from LVI, MVI or HVI neutral lubricating oils of a synthetic sulfonate. As used herein, VI represents viscosity index and L, M and H represent low, medium and high. The term "equivalent weight" as used herein has its usual meaning, i.e., the equivalent of a substance in grams, which is calculated by dividing its formula weight (molecular weight) by the valence of its metal atom. For example, the equivalent weight of a calcium sulfonate is one-half its molecular weight, whereas the molecular weight and equivalent weight of a sodium sulfonate are the same. Accordingly, calcium sulfonates are often classified by their equivalent weight which is approximately the same as the equivalent weight or molecular weight of the corresponding sodium sulfonate.

The neutral oils which may be used to prepare a low molecular weight petroleum sulfonate may be obtained from a variety of natural oils such as paraffinic, naphthenic and mixed base crudes. Preferably, the neutral oils for use in preparing the low molecular weight petroleum sulfonates are LVI, MVI and HVI neutrals having viscosities of from 100 to 2000 SSU at 100° F. and average molecular weights of from 250 to 500. Examples of suitable neutral oils include oils having the following properties:

TABLE 1

Property	A	B	C	D	E
Gravity, ° API	24.7	21.7	22.8	22.5	30.0
Color, ASTM	L1.5	L2.5	1.5	2.0	L1.6
Pour Point, ° F	0	0	−40	−20	10
Flash COC° F	480	440	325	415	430
Fire, ° F	540	500	360	455	500
Viscosity:					
SSU at 100° F	1,250	1,080	106	557	265
SSU at 210° F	82.5	71.2	38.2	55.8	50
Viscosity Index	55.0	25	-------	25	93
Neutral, TBN–E					
Acid Neutralization Number	0.025	0.03	(1)	0.03	0.1

[1] Neutral.

The ratio of the low molecular weight sulfonate component of the additive to the high molecular component is from 0.1:1.0 to 0.3:1.0.

The high molecular weight sulfonate component of the additive has an average equivalent weight of at least 700, and preferably from 725 to 900, and may be a petroleum sulfonate prepared from bright stock or a synthetic sulfonate.

Bright stock oil fraction is a viscous product refined by solvent extraction, hydrotreated, and then dewaxed. The viscosity of the bright stocks vary from about 80 to 250 SSU at 210° F. Bright stock used to prepare the additive of the present invention has an average molecular weight range of from about 650 to 900, or higher.

The high and low molecular weight petroleum sulfonates which may be used in forming the additive are conveniently prepared by (1) sulfonation of the base stock with a sulfonating agent, such as sulfur trioxide, chlorosulfonic acid or oleum (fuming sulfuric acid) and preferably the sulfonating agent is fuming sulfuric acid; (2) separation of the sulfonic acid; (3) neutralization of the acid with a hydroxide, such as calcium or sodium, prefreably calcium, to yield a slightly basic sulfonate; and finally (4) carbonation of the sulfonate in the presence of excess of an alkaline earth metal hydroxide, such as barium or calcium hydroxide, to yield the highly basic alkaline earth metal petroleum sulfonate.

The high and low molecular weight synthetic sulfonates which may be used in forming the additive include those described in U.S. Patent No. 3,250,710 and Canadian Patent No. 733,142. Thus, the oil-soluble synthetic sulfonates, such as calcium sulfonates, can be of the cyclic or aliphatic type. The cyclic sulfonates include the mono- or poly-nuclear aromatic or cycloaliphatic sulfonates. The synthetic sulfonates can be represented by the following formulas:

$$[R_x—T—(SO_3)_y]_zM_b$$

$$[R'—(SO_3)_a]_dM_b$$

wherein M is calcium, T is a cyclic nucleus such as, for example, benzene, naphthalene, enthracene, phenanthrene, diphenylene oxide, thianthrene, phenothioxine, diphenylene sulfide, phenothiazine, diphenyl oxide, diphenyl sulfide, diphenylamine, cyclohexene, petroleum naphthenes, decahydronaphthalene, cyclopentane, etc.; R is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, carboalkoxyalkyl, etc.; x is at least 1, and R_x—T contains a total of at least about 15 carbon atoms. R′ is an aliphtic radical containing at least about 15 carbon atoms. Examples of types of the R′ radical are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R′ are saturated and unsaturated paraffin wax, and polyolefins, including polymerized C_2, C_3, C_4, C_5, C_6, etc., olefins having molecular weights from 200 to 1000. The groups T, R, and R′ in the above formulas can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfides, disulfide, etc. In the above formulas y, z, a, b and d are also at least 1.

Specific examples of oil-soluble synthetic sulfonates are the calcium salts of mono- and polywax substituted sulfonic and polysulfonic acids of, e.g., naphthalene, phenol, diphenyl ether, naphthalene disulfide, dipenylamine, thiophene, alpha-chloronaphthalene, etc.; other substituted sulfonic acids such as cetyl chlorobenzene sulfonic acids, cetylphenol mono-sulfide sulfonic acids, cetoxy caprylbenzene sulfonic acids, dicetyl thianthrene disulfonic acids, dilauryl beta-naphthyl sulfonic acids, dicapyryl nitronaphthalene sulfonic acids, and alkaryl sulfonic acids such as dodecyl benzene "bottoms" sulfonic acids (i.e., those acids derived from benzene which has been alkylated with propylene tetramers or isobutene trimers to introduce 1, 2, 3, or more branched-chain C_{12} substituents on the benzene ring. Dodecyl benzene bottoms, principally mixtures of mono- and di-dodecyl benzenes, are available as byproducts from the manufacture of household detergents) and mono- and poly-tridecyl benzenes; aliphatic sulfonic acids such as paraffin wax sulfonic acid, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic acids, hexapropylene sulfonic acids, tetraamylene sulfonic acids, nitro-paraffin wax sulfonic acids, etc.; cycloaliphatic sulfonic acids such as petroleum naphthene sulfonic acids, cetyl cyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, bis(diisobutyl)cyclohexyl sulfonic acids, mono- or poly-wax substituted cyclohexyl sulfonic acids, etc. The synthetic sulfonates are then carbonated in the same manner as the petroluem sulfonates.

Examples I and II are illustrative of a method of preparing the subject sulfonates.

EXAMPLE I

Procedure Ia

A high molecular weight petroleum sulfonate was prepared by charging a 3-liter, 3-necked round-bottom flask equipped with stirrer, dropping funnel, thermometer and vent with 1 kg. West Texas Ellenburger bright stock (hereinafter referred to as oil F) having the following properties:

Viscosity at 100° F., SSU	2812
Viscosity at 210° F., SSU	116.1
Viscosity index	99
Sulfur, percent by weight	0.07
Molecular weight	770
Total aromatics, percent by weight	40
Monoaromatics, percent by weight	28.1

The stock was stirred vigorously and 105 percent by weight sulfuric acid (200 g., 20 percent by weight oleum) was added dropwise during one hour; the temperature rose from 25° to 45° C. The mixture was stirred an additional 30 minutes and then 15 ml. of water was added with stirring. The mixture was diluted with a volume of hexane equal to the volume bright stock charged (1132 ml.) and allowed to stand overnight. A small amount of spent acid (86 ml., 149 g.) separated which was dark brown, quite fluid and easily handled. The hexane layer was washed with a solution of 500 ml. of water and 750 ml. methanol. The clear yellow lower layer that separated was discarded. The upper layers was shaken with 750 ml. absolute methanol. Two phases formed and separated completely in two hours. The lower sulfonic acid layers was withdrawn, diluted with 1 liter of n-hexane and shaken with a solution of 68 g. of sodium hydroxide in 500 ml. water. The two phases were separated. The aqueous phase was discarded and the hexane layer was stripped of solvent and water with nitrogen under vacuum. The residue which was sodium sulfonate concentrate weighed 520 g.

550 g. of sodium sulfonate prepared by the procedure just described was stirred with a solution of 700 g. of calcium chloride and 100 g. of calcium hydroxide in 2270 ml. water for 4 hours at about 90° C. 10 kg. toluene was added and the water was removed by azeotropic distillation using a water trap. The mixture was cooled to 55° C. and a mixture of 294 g. calcium hydroxide, 4.4 g. benzoic acid and 1050 g. methanol was added thereto. The resulting mixture was stirred at 55° C. while 88 g. carbon dioxide was bubbled in. The solvents were stripped off and the mixture was filtered. The product was a highly basic Ca petroleum sulfonate (hereinafter referred to as sulfonate FF) having an average equivalent weight of 750, a 8.3% sulfated ash content and a TBN–E (total base number) of 45.6.

Procedure Ib

Alternatively, the sulfonic acid layer, present after extraction with 750 ml. of absolute methanol in Procedure Ia, can be neutralized with calcium hydroxide in aqueous slurry by stirring with 250 ml. water and 74 g. calcium hydroxide for 5 minutes, separating the neutralized product and treating as before with calcium hydroxide, benzoic acid, methanol and carbon dioxide.

The following examples are for purposes of illustrating the invention and are not intended to limit the invention to the particular compounds and compositions described.

EXAMPLE II

The procedure of Example Ia was repeated with the exception that 1 kg. of an LVI 60/210 neutral oil, designated hereinbefore as oil D in Table 1, was used as the sulfonate feed in place of the bright stock of Example Ia. The resulting highly basic Ca petroleum sulfonate (sulfonate DD) had an average equivalent weight of 470. Similarly, highly basic sulfonates AA, BB, CC and EE were also prepared from oils A, B, C and E of Table 1, respectively.

EXAMPLE III

This example illustrates the influence of sulfonate molecular weight on rust protection as determined in the severe Falcon Engine Rust Tests. This test is described in detail in Ghannam's SAE Paper No. 650,869, presented at Tulsa, Okla., Nov. 2–4, 1965 meeting. The results of the test are given in Table 2.

TABLE 2.—FALCON-ENGINE RUST TEST

	Oil		
Sulfonation Feed	D	A	F
Sulfonate equivalent wt	470	540	750
Formulation, Percent w.:			
Sulfonate, percent w. sulfated ash	1.2	1.2	1.2
Succinimide [1]	1.0	1.0	1.0
Sinc dithiophosphate [2]	3.4	3.4	3.4
Acryloid 150 [3]	0.5	0.5	0.5
Balance mineral oil			
Rust Rating (10=no rust):			
Valve lifters	9.8	9.0	7.0
Overall	9.8	8.9	7.5

[1] Polyisobutenyl succinimide of tetraethylene pentamine.
[2] Sinc bis(octylphenyl) dithiophosphate.
[3] Methacrylate polymer.

The data of Table 2 show that as the molecular weight of the sulfonates increase the rust protection afforded thereby decreases.

Although the rust protection provided by the low molecular weight sulfonate is acceptable, the cleanliness provided thereby is not good. Cleanliness properties of formulations containing sulfonates of various molecular weights is illustrated in Example IV.

EXAMPLE IV

This example illustrates the influence of sulfonate molecular weight on engine cleanliness as determined by MS Sequence V Engine Test which was designed to evaluate engine deposits produced by low and medium temperature operating conditions with emphasis on anti-sludging, anti-clogging, and insoluble suspension characteristics of engine lubricants. The test engine is a 368 cu. in. Lincoln; the test fuel is a conventional summer grade regular gasoline. The test conditions are in general:

[Duration—192 hrs. (48 cycles, 4 hrs.)]

Time	Load	Speed, r.p.m.	Water, °F.	Oil, °F.	Air/fuel
45	None	500	115	125	9.5 (rich).
120	Approx. ⅔	2,500	125	175	15.5 (lean).
75	Approx. ⅔	2,500	170	205	15.5 (lean).

After 48 cycles without oil drain, the engine is disassembled and inspected. Sulfonates EE, FF, BB and GG were evaluated in the Sequence V Test at a 1.2 percent by weight sulfated ash level and using an oil of the following formulation:

	Percent by wt.
Sulfonate (sulfated ash)	1.2
Polyisobutenylsuccinimide of tetraethylene pentamine	1.0
Zinc bis(octylphenyl)dithiophosphate	3.4
SAE 10W motor oil	Balance

The results of the test are given in Table 3.

TABLE 3.—SEQUENCE V CLEANLINESS TEST

		Oil				
		D	D (tail) [1]	E	A	F
	Ford Requirement	Sulfonation feed, sulfonate mol. wt.				
Seq. V Cleanliness Rating		470	480	504	540	720
Overall sludge (50=clean)	>30	26.5	34.9	38.8	42.3	48.7
Piston lacquer (10=clean)	>7	7.0	8.2	8.2	9.0	9.7
Overall lacquer (50=clean)		27.0	38.5	42.3	44.8	48.6
Oil screen plugging, percent	<30	90	5	1	5	1
Oil ring plugging, percent	<30	60	61	2	2	0

[1] D (tail) is oil D which has been topped to remove some of the lighter ends, thereby increasing the average molecular weight of the oil.

The data of Table 3 show that as the molecular weight of the sulfonates increases the engine cleanliness provided thereby also increases, however, as shown in Table 2 the rust protection provided by the high molecular weight sulfonates is unacceptable.

It is unexpectedly discovered that by blending a small amount of the low molecular weight sulfonates (equivalent wt. 450–550) with the high molecular weight sulfonates (equivalent wt. ≥740) an additive is provided which imparts both cleanliness and rust protection to the lubricating oil. This result is illustrated in Example V.

EXAMPLE V

A blend of sulfonates DD and FF (blend DF) was prepared whereby the blend had a sulfated ash level of 1.2 percent by weight of which sulfonate DD provided 0.2% thereof and sulfonate FF provided 1.0 percent by weight. The sulfonate blend was incorporated into a formulation for purposes of comparing its performance in the Falcon Rust Test and the Sequence V Test, respectively, with the sulfonates previously tested therein.

Formulation X

Blend DF, percent by weight sulfated ash	1.2
Polyisobutenyl succinimide of tetraethylene pentamine	None
Zinc bis(octylphenyl)dithiophosphate	3.4
Acryloid 150	0.5
Mineral oil	Balance

Formulation X is the same as the formulations used in the previous Falcon Rust Test (Example III) and Sequence V Test (Example IV) with the exception of the particular sulfonates and that Formulation X does not contain the succinimide (dispersant).

The results of these tests are given in Table 4.

TABLE 4

Sequence V Engine Tests

Seq. V ratings:	Formulation X
Overall sludge, 50=clean	47.2
Overall lacquer, 50=clean	47.5
Oil ring clogging, percent	0
Oil screen clogging, percent	1

Falcon-Rust Engine Tests

Rust rating, 10=no rust:	Formulation X
Valve lifters	9.7
Overall	9.3

The data of Table 4 establish that blend DF provides both good engine rust protection and good engine cleanliness, whereas the individual sulfonates at the same sulfated ash level provide either good rust protection or good cleanliness, but not both. This result is unexpected at the concentrations of the individual sulfonates comprising the additive, since it would be expected that a higher concentration of the low molecular weight sulfonate would be required to afford adequate rust protection. The benefit of the necessity of using only a small amount of the low molecular weight sulfonate in the blend is that greater cleanliness can be attained, owing to the higher concentration of the high molecular weight sulfonate on the one hand and the lower concentration of the low molecular weight sulfonate on the other hand. Moreover, the sulfonate blend also has good dispersancy properties as demonstrated in Table 4, Formulation X.

EXAMPLE VI

A blend of synthetic sulfonates is prepared from (1) carbonated calcium sulfonate of postdodecylbenzene (constitutes a mixture of dodecylbenzene and didodecylbenzene in approximate molar ratio of 2.3) and (2) carbonated calcium sulfonate of polyisobutene sulfonic acids having an average equivalent weight of about 750, wherein the blend contains (1) and (2) in the weight ratio of 5 to 1. A formulation is then prepared containing 97% by weight of mineral oil and 3% by weight of the blend.

The sulfonate blend of the present invention may be incorporated into mineral lubricating oil obtained from paraffinic, asphaltic or mixed base crudes and/or mixtures thereof, for example, a neutral oil having a viscosity which may vary over a wide range such as from 100 to 2000 SSU at 100° F. Under extreme engine operating conditions it is desirable to use an oil blend containing from 1 to 20% of bright stock having a viscosity of from 80 to 250 SSU at 210° F. and a range in molecular weight from about 500 to 2000 or higher. In addition to mineral lubricating oils, the adduct additives may be incorporated into synthetic lubricating oils such as polymerized olefins, esters and others. Mixtures of natural and synthetics can also be used.

The additives of this invention can be used effectively in any of the above oily media in amounts of from 0.1% to 20% by weight and preferably from 2% to 13% although amounts as large as 30% or as little as 0.01% by weight may effectively be incorporated into oils under certain circumstances.

Other additives may also be incorporated into lubricating compositions in addition to the sulfonate blend of the present invention such as any of the additives recognized in the art to perform a particular function or functions, i.e., pour point depressants and viscosity index improvers, e.g., methacrylate polymers (Acryloid 150); dispersants, e.g., nitrogen-containing compounds such as the polyisobutenyl succinimide of polyethyleneamine, copolymers of

vinyl pyridine with at least one acrylate ester or a vinyl pyrrolidone copolymer; anti-oxidants, e.g., amines, phosphorus or phenolic compounds, i.e., phenyl-alpha-naphthylamine, zinc dialkyldithiophosphates, or 4,4'-methylene-bis(2,6-di-t-butylphenol); anti-foam agents; corrosion inhibitors and the like.

The compoistions described herein can be used as motor oils, gear oils and in various other applications where cleanliness, rust protection, and detergency are desirable.

We claim as our invention:

1. A lubricant consisting essentially of a major amount of a lubricating oil and a minor amount, sufficient to impart rust inhibition and detergency, of a blend of low molecular weight and high molecular weight highly basic alkaline-earth metal petroleum sulfonates wherein:
   (1) the petroleum sulfonates have a basicity of at least 40%;
   (2) the low molecular weight petroleum sulfonate component of the blend has an average equivalent weight of from 450 to 550;
   (3) the high molecular weight petroleum sulfonate component of the blend has an average equivalent weight of from 700 to 900; and
   (4) the ratio of the low molecular weight component to the high molecular weight component is from 0.1–1.0 to 0.3–1.0.

2. A lubricant as defined in claim 1 wherein the sulfonates have a basicity of from 100% to 800%

3. A lubricant as defined in claim 1 wherein the alkaline earth metal is calcium.

4. A lubricant as defined in claim 1 wherein the high molecular weight sulfonate is prepared from bright stock having an average molecular weight of from about 650 to about 900.

5. A lubricant as defined in claim 1 wherein the low molecular weight sulfonate is prepared from a lubricating oil which is a neutral oil having a viscosity of from about 50 to 80 SSU at 210° F.

6. A lubricant as defined in claim 1 wherein the ratio of low to high molecular weight sulfonates is about 0.2 to 1.0.

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