

1

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## HEAVY DUTY LUBRICANTS

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This invention relates to highly detergent heavy duty lubricants. More particularly, the present invention relates to new and novel heavy duty lubricating oil compositions which also possess good stability as well as corrosion and wear inhibiting properties.

It is known that to effectively maintain heavy duty engines such as diesel and truck engines clean and in good operating conditions that such engines should be lubricated with lubricants containing metallic detergents such as polyvalent metal organic sulfonates. Because of their tendency to form ash and abrasive deposits, attempts have been made to replace metal-containing detergents with non-ash forming polymeric detergents as has been successfully accomplished with automotive lubricating composition. However, it appears that non-ash-containing detergents lack sufficient detergent power to make them useful in lubricants designed for heavy duty purpose.

It has now been discovered that a particular class of non-ash polymeric detergents can be sufficiently activated so as to provide them with detergent power suitable for use in heavy duty lubricants, by addition to such lubricants, a small amount of a mixture (A) which consists of (1) from 1% to 10% of a complex barium-zinc salt of a sulfonic acid and a reaction product of phosphorus sulfide and an olefin (2) from 0.1% to 1% of an oil-soluble divalent metal alkyl dithiocarbamate, and (3) from 5% to 30% bright stock. The amounts of each activating component in the mixture may be as follows: The novel non-ash polymeric detergent which when activated by mixture (A) can be used for heavy duty purposes is generally added to lubricating oils such as mineral lubricating oil in amounts of from 2% to 8% preferably between 4% and 6%. All of the above values are by weight percent.

The polymeric detergent of this invention is an oil-soluble copolymer of a cyclic amido (lactam) compound such as N-vinyl butyrolactam and another copolymerizable organic compound such as an unsaturated ester, or mixtures thereof. Examples of N-vinyl butyrolactams include N-vinyl pyrrolidone, N-1-methylvinyl pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3,3-dimethyl pyrrolidone, N-vinyl-5-ethyl pyrrolidone, N-vinyl-4-butyl pyrrolidone, N-ethyl-3-vinyl pyrrolidone, N-butyl-5-vinyl pyrrolidone, N-vinyl-5,5-dimethyl pyrrolidone, N-vinyl-3,3-dimethyl-5-methoxy pyrrolidone, 3-vinyl pyrrolidone, 4-vinyl pyrrolidone, 5-vinyl pyrrolidone and 5-cyclohexyl-N-vinyl pyrrolidone. Other N-vinyl-cyclic nitrogen-containing compounds are N-vinyl piperidone, N-vinyl-6-methyl piperidone, N-vinyl-3-methyl piperidone, N-(1-methylvinyl) piperidone, N-methyl-6-vinyl piperidone and N-vinyl caprolactam and the like.

The other copolymerizable materials include unsaturated esters of unsaturated acids, e.g. acrylic or methacrylic acids and long-chain alkanols, e.g. C<sub>12-18</sub> alkanols. Esters of this type include, lauryl acrylate, lauryl methacrylate, stearyl acrylates, stearyl methacrylate, cetyl methacrylate, and mixtures thereof.

The copolymers can be prepared by a suitable means preferably in the presence of a polymerization initiator such as a peroxide or azo compound, in the presence or absence of an inert solvent, such as a hydrocarbon, under a blanket of an inert gas, such as nitrogen or carbon dioxide, and at a temperature ranging from ambient room

2

temperature (about 20° C.) or lower, to about 180° C. or higher, preferably from 50° C. to 150° C., for a period of from about 2 to 28 hours, giving molecular weights of the polymer varying from 200,000 to 600,000 and preferably ranging from 300,000 to 450,000. The molecular weight of the polymers is determined by the light scattering technique described in Chemical Reviews, volume 40, page 319 (1948).

Various combinations of conditions may be employed to maintain the molecular weight within the desired range. Factors which exert an influence on the molecular weight of the polymer include the method of polymerization (e.g. polymerization in emulsion, suspension, solvent solution of bulk, the nature and concentration of the catalyst employed, the temperature, and nature and amount of the particular monomers. When the polymerization is accomplished in solution, the molecular weight of the product will be lower when the dilution is higher, e.g. when the proportion of solvent is greater. With the same catalyst, the higher polymerization temperature tends to give low molecular weight polymers.

The following examples illustrate the preparation of suitable polymers for use in oil compositions in accordance with the invention.

## EXAMPLE I

A mixture of about 2 mols of lauryl methacrylate, 1 mol of N-vinyl pyrrolidone and 0.5% by weight of benzoyl peroxide was reacted in a suitable reaction vessel for a period of about 10 hours at about 65° C. The polymer was then dispersed in benzene and thereafter precipitated with a mixture of acetone and methanol. A copolymer of lauryl methacrylate/N-vinyl pyrrolidone having a nitrogen content of 2.20% by weight and a molecular weight in excess of 250,000 was recovered. The polymer contained the monomer units essentially in the mol ratio as provided in the mixture; it had an alkane chain of about 2400 carbon atoms carrying about 800 lauryl-oxyformyl groups and about 400 butyrolactam groups.

## EXAMPLE II

A copolymer of lauryl methacrylate and N-vinyl pyrrolidone was prepared by the method of Example I with the same monomer ratio but in which 0.75% by weight of alpha,alpha-azodiisobutyronitrile was used as the catalyst. The molecular weight of the polymer was around 225,000.

## EXAMPLE III

A terpolymer of stearyl methacrylate/lauryl methacrylate/N-vinyl pyrrolidone in the mole ratio of 2.8/5.6/1, respectively, was prepared essentially by the method of Example I using 0.2% alpha,alpha-azodiisobutyronitrile as catalyst and the reaction time was 48 hours. The polymeric product was oil-soluble and had an average molecular weight over  $1 \times 10^4$  as determined by the light scattering technique.

## EXAMPLE IV

When a copolymer of stearyl methacrylate/N-vinyl piperidone, in which the reactants are in a mol ratio of 4:1, respectively, is prepared essentially by the method of Example I, the obtained polymer is oil-soluble and contains the monomer units in the ratio of about 4:1, respectively.

Other representative examples of copolymers include: copolymer of N-vinyl pyrrolidone/cetyl fumarate/stearyl fumarate, copolymer of N-vinyl pyrrolidone/lauryl fumarate, copolymer of N-vinyl pyrrolidone/vinyl stearate, copolymer of N-vinyl pyrrolidone/dodecene-1/lauryl methacrylate, copolymer of N-vinyl pyrrolidone/lauryl

fumarate/lauryl methacrylate, copolymer of N-vinyl piperidone/lauryl methacrylate, copolymer of N-vinyl caprolactam/lauryl methacrylate.

The barium-zinc complex salt which is one of the components of mixture (A) is a complex barium-zinc salt of a reaction mixture of a sulfonate and a phosphorus sulfide treated olefin such as polyisobutylene, terpene or simple olefins such as methyl butene-1, pentene-2 and the like. Various known methods can be used to prepare the complex salt. Thus, the anionic portion of the salt, namely the interaction between the phosphorus sulfide-olefin reaction product and the sulfonate is carried out in the presence of a phenolic promoter such as C<sub>1-12</sub> alkyl phenol, the reaction mixture neutralized with a barium and zinc compound such as an oxide, hydroxide or carbonate of barium and zinc and thereafter blown with an acidic material such as air or carbon dioxide. The procedures such as described below can be followed to form the barium-zinc complex salts and the following examples are illustrative of such complexes.

#### EXAMPLE A

About 5 moles of polyisobutylene (M.W. 750) was reacted with an excess of a mixture of P<sub>2</sub>S<sub>5</sub> and S (7:1) at about 210–220° C. for about 2 hours after which the reaction product was diluted with mineral oil, heated for another 2 hours, air blown and filtered. About 1 equivalent of the filtered phosphorus-sulfur containing polyisobutylene was admixed with an excess of mixture Ba(OH)<sub>2</sub>, Zn(OH)<sub>2</sub> in the presence of a small amount of water under reflux conditions at first and after about 2 hours the temperature increased to 150°–170° C. to drive off the water. To the mixed Ba–Zn salt is added about 4 equivalents of a mixture (50/50) phenol and its Ba salt and about 0.5 equivalent of barium-zinc petroleum sulfonate and the entire mixture refluxed for 2–4 hours at 100–250° C. after which it is blown with CO<sub>2</sub> for about 1–2 hours and heated for about 1–2 hours at 200–220° C., cooled and filtered to recover an end product containing 10–16% Ba, 1–2% Zn, 0.5–5% P, 1–10% S and a base number above 7.5 (10–20).

Other complex prepared essentially by the process of Example I include:

#### EXAMPLE B

Ba–Zn complex salt of petroleum sulfonate and P<sub>2</sub>S<sub>5</sub>-polyisobutylene reaction product.

#### EXAMPLE C

Ba–Zn complex salt of petroleum sulfonic acid and P<sub>2</sub>S<sub>5</sub>-hexene reaction product.

#### EXAMPLE D

Ba–Zn complex salt of petroleum sulfonate and P<sub>2</sub>S<sub>5</sub>-terpene reaction product.

#### EXAMPLE E

Ba–Zn complex salt of petroleum sulfonate, alkyl phenol and P<sub>2</sub>S<sub>5</sub>-polyisobutylene reaction product.

Products of this type are available from Lubrizol Corporation under the trade name Lubrizol 1402 and Lu-

brizol 1442 (referred to hereinafter as Examples F and G, respectively), have the following properties.

Percent wt.	Example F	Example G
Ba.....	11.3	12.05
P.....	2.2	1.78
S.....	4.3	2.96
Zn.....	1.9	1.57

The second activator of mixture (A) is an oil-soluble Ca, Ba, Zn or Cd dialkyl dithiocarbamate such as Ca, Ba, Zn or Cd dipropyl dithiocarbamate, dibutyl dithiocarbamate, diamyl dithiocarbamate, dihexyl dithiocarbamate, dioctyl dithiocarbamate, di-2-ethylhexyl dithiocarbamate, diisobutyl dithiocarbamate, diisoamyl dithiocarbamate, N-amyl-N'-methyl dithiocarbamate, N-methyl-N-octyl dithiocarbamate, N-octyl-N'-butyl dithiocarbamate, N-n-amyl-N'-2-methylbutyl dithiocarbamate, N-n-amyl-N'-3-methylbutyl dithiocarbamate, N-octyl-N'-2-ethylhexyl dithiocarbamate, N-ethyl-N'-phenyl dithiocarbamate, dicyclohexyl-dithiocarbamate, diphenyl dithiocarbamate, and the like as well as mixtures of these salts. The preferred are the Zn and Cd dibutyl or diamyl or di-2-ethylhexyl dithiocarbamates.

The third component of mixture (A) is a bright stock. The term bright stock is well known in the petroleum art and is highly viscous residual petroleum fraction having a viscosity at 210° F. in the range of from 125 to 325. To obtain the desired fraction, crude oils are usually subjected to distillation under ordinary pressures in order to obtain a "long residue" comprising the fraction which does not distill under these conditions without substantial decomposition. The long residue is then subjected to steam distillation, usually under a vacuum. Under these conditions, gas oil and waxy lubricant fractions distill over, leaving what is normally termed a "short residue" or a "steam refined stock," also known as "cylinder stock." The steam refined stock is then dewaxed and deasphalted (if an asphaltic crude is employed). Following this, the raffinate is treated with a solvent for the purpose of reducing or removing the aromatic fractions. Clay contact treatment or percolation may be employed to clean up the oil following any one or all of these separate operations. The raffinate which remains after deasphalting, dewaxing, extraction, and clay treatment is generally called "bright stock."

The bright stocks should have the following ranges of properties:

#### Properties of bright stocks

Viscosity, SUS 100° F. >1250, usually 1250–11,000, preferably 1500–3500.

Viscosity, SUS 210° F. >75, usually 125–325, preferably 150–250.

Viscosity index, >+60, preferably +85–110.

Aniline point, >100, preferably >115.

Flash, ° F., >475, preferably >500.

Fire, ° F., >550, preferably >600.

Pour point, (° F.), +25 maximum, preferably lower than +15°.

Percent aromatics, <15, preferably <10 opt. <5.

TABLE I.—EXAMPLES OF TYPICAL BRIGHT STOCKS

	SUS		Viscosity Index	Aromatic	Ring Analysis		Ratio of Paraffines to Naphthenes	Average Mol Weight	Average Rings per Mol
	100	210			Naphthenes	Paraffines			
Mid-Continent Bright Stock, Conventional Extraction.....	3,650	164	77	13	17	70	4.1	685	3.7
Mid-Continent Bright Stock, Mild Extraction.....	2,569	141	85	9	19	72	3.8	685	3.4
Mid-Continent Bright Stock, Heavy Extraction.....	2,049	131	93	3	21	76	3.62	675	2.9
Pennsylvania Bright Stock.....	2,109	144	102	5	16	79	4.95	790	3.0
Coastal Bright Stock.....	1,251	85	63	4	35	61	1.74	515	3.4

Percent naphthenes, <35.

Percent paraffins, at least 60.

The tables which follow give the properties of typical bright stocks which are useful in the compositions of this invention.

Typical bright stocks have the following properties:

TABLE II.—SPECIFICATIONS FOR TYPICAL MID-CONTINENT BRIGHT STOCKS (U, V, W)

	Unfiltered		Filtered	
	U	V	W	Houston Bright Stock X
Gravity, ° API, minimum	25.5	24.5	25.5	26.6
Color, NPA	8+	Dark green	6.7	6+
Pour Point, ° F., maximum	10	10	10	0
Flash, ° F., minimum	540	580	545	550-570
Fire, ° F., minimum	615	655	610	
SUS 210° F	150-170	200-215	150-160	150-160
Viscosity Index, minimum	90	90	90	90-92

The mineral lubricating oils used in compositions of this invention can be obtained from any paraffinic, naphthenic, asphaltic or mixed base crude, and/or mixture thereof. The viscosity of these oils may vary over wide range such as from 100 SUS at 100° F. to 100 SUS at 210° F.

Mineral lubricating oils which are particularly desirable for use in compositions of the invention can be obtained from West Texas Ellenburger crudes, East Texas crudes, Oklahoma crudes, California crudes having a viscosity range of 150-450 SUS at 100° F. and a viscosity index between 90 and 95.

The following are examples of compositions of the present invention.

Composition A:	Percent wt.
Example I copolymer	4.0
Example A additive complex	5.5
Zn diamyl dithiocarbamate	0.5
Bright stock (150 SUS 210° F.)	20
Mineral lubricating oil (20W-40)	Bal.

Composition B:	Percent wt.
Example III copolymer	2
Example A additive complex	4.5
Zn diamyl dithiocarbamate	0.5
Bright stock (150 SUS 210° F.)	16
Mineral lubricating oil	Bal.

Composition C:	Percent wt.
Example I copolymer	4.0
Lubrizol 1402 additive complex	5.5
Zn diamyl dithiocarbamate	0.5
Bright stock (150 SUS 210° F.)	20
Mineral lubricating oil (20W-40)	Bal.

Composition D:	Percent wt.
Example I copolymer	4.0
Lubrizol 1455 additive complex	5.5
Zn diamyl dithiocarbamate	0.5
Bright stock (150 SUS 210° F.)	20
Mineral lubricating oil (20W-40)	Bal.

Compositions of the present invention were tested under various conditions and compared with other types of non-ash containing oils and the superiority of compositions of the present invention is clearly evident by reference to the data presented in the following tables.

TABLE III.—CATERPILLAR L-1 ENGINE TEST (1% S FUEL, 480 HOURS)

Composition	Top-Groove Filling, Percent	Cleanliness Rating (100=Perfect)
A	14	96.9
C	14	97.0
XX*	37 (240 hours)	91.7

\*XX=Example I copolymer in Composition A replaced with 4% copolymer of 2-methyl-5-vinyl pyridine/lauryl methacrylate/stearyl methacrylate (MW 650,000). Test stopped because of excessive sludge after 240 hours.

TABLE IV.—200 HOUR IHC HEAVY DUTY GASOLINE ENGINE TEST (100=PERFECT)

Composition	Piston Lacquer	Ring Land Deposits	Oil Ring Plugging, Percent	Gray Paint	Overall Cleanliness Rating
A	92-95	Light	0	None	99
C	92-95	do	0	do	99
YY*	80	Heavy	17	Med. heavy	94

\*YY=Same as Composition A but Example A complex replaced with 5.5% basic Ca petroleum sulfonate.

TABLE V.—30,000 MILE CHEVROLET ENGINE OPERATED UNDER HEAVY DUTY TRUCK SERVICE CONDITIONS (100=PERFECT)

Composition	Lacquer Rating	Sludge Rating	Oil Ring Plugging, Percent	Overall Cleanliness Rating
A	94	98	6	96
ZZ*	56	88	50	72

\*ZZ=Mineral oil+7.65% Base Ca petroleum sulfonate+3.26% Ca octyl phenol-formaldehyde condensation product+0.66% Zn dialkyl dithiophosphate+0.1% C<sub>18</sub> alkylamine.

The additive combination of this invention is useful for providing superior detergent and wear inhibiting properties to lubricating oils which contain small amounts (0.1% to 3%) of other agents such as metal dithiophosphates (Zn alkyl dithiophosphate) viscosity-index improvers and pour point depressants such as the "Acryloids," and specifically, "Acryloid," 15, 618, 710, and/or 768, made by Rohm & Haas and described in U.S. Patent 2,710,842; condensation products of chlorinated paraffin wax and naphthalene; extreme pressure agents such as amine salts of thiochloromethane phosphonic acid, organic sulfides and mixtures thereof.

Compositions of this invention can be also used as turbine oils, gear oils, and in various other fields of lubrication where detergency and wear inhibiting properties are essential.

We claim as our invention:

1. A heavy duty lubricating composition comprising a major amount of mineral lubricating oil and (I) from 2% to 8% of an oil-soluble copolymer of N-vinyl pyrrolidone and a C<sub>8-18</sub> alkyl methacrylate in the mol ratio of about 1:4 respectively, and having a molecular weight of from about 200,000 to about 600,000, and (II) a mixture of from about 5% to about 30% bright stock, from about 0.1% to about 1% of Zn dialkyl dithiocarbamate the alkyl radicals having from 1 to 5 carbons atoms and from about 1% to about 10% of a complex Ba-Zn salt of petroleum sulfonate and P<sub>2</sub>S<sub>5</sub>-polyisobutylene reaction product.

2. A heavy duty lubricating composition comprising a major amount of mineral lubricating oil and (I) from 2% to 8% of an oil-soluble copolymer of N-vinyl pyrrolidone and lauryl methacrylate in the mol ratio of about 1:4 respectively, and having a molecular weight of from about 200,000 to about 600,000, and (II) a mixture of from about 5% to about 30% bright stock, from 0.1% to about 1% of Zn diamyl dithiocarbamate and from about 1% to about 10% of a complex Ba-Zn salt of petroleum sulfonate and P<sub>2</sub>S<sub>5</sub>-polyisobutylene reaction product.

3. A heavy duty lubricating composition comprising a major amount of mineral lubricating oil and (I) from 2% to 8% of an oil-soluble copolymer of N-vinyl pyrrolidone and stearyl methacrylate in the mol ratio of about 1:4 respectively, and having a molecular weight of from about 200,000 to about 600,000, and (II) a mixture of from about 5% to about 30% bright stock, from 0.1% to about 1% of Zn diamyl dithiocarbamate and from about 1% to about 10% of a complex Ba-Zn salt of petroleum sulfonate and P<sub>2</sub>S<sub>5</sub>-polyisobutylene reaction product.

4. A heavy duty lubricating composition comprising a major amount of mineral lubricating oil and (I) from 2% to 8% of an oil-soluble copolymer of N-vinyl pyrrolidone and a mixture of stearyl methacrylate and lauryl methacrylate in the mol ratio of 1/2.8/5.6 respectively, and

having a molecular weight of from about 200,000 to about 600,000, and (II) a mixture of from about 5% to about 30% bright stock, from 0.1% to about 1% of Zn diamyl dithiocarbamate and from about 1% to about 10% of a complex Ba-Zn salt of petroleum sulfonate and P<sub>2</sub>S<sub>5</sub>-polyisobutylene reaction product.

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