

1

2,916,449

LUBRICATING COMPOSITIONS

Ernest R. Vierk, Lansing, Ill., and Theodore J. Karr, East Chicago, Ind., assignors to Sinclair Refining Company, New York, N.Y., a corporation of Maine

No Drawing. Application July 22, 1957
Serial No. 673,110

12 Claims. (Cl. 252-32.7)

This invention relates to lubricants and is particularly concerned with a new lubricant composition which is especially advantageous as a paper machine circulating system oil.

The dryer end of modern Fourdrinier paper machines contains, on the average, 50 to 100 hollow cast iron cylinders which are heated internally by steam. The presence of this steam and the inevitable pulp and paper bits presents an important lubrication problem in this field. The natural construction of these machines renders the parts which must be lubricated and contacted by lubricating oil inaccessible. Consequently, it has become conventional to design an automatic lubrication system into the machine. The automatic lubrication system, known as the oil circulating system, normally comprises an oil reservoir, lubrication lines to the bearings, side gears, etc., a means for settling, filtering and purifying the oil. The oil employed has three main functions, these being lubrication, cooling and flushing.

Conditions obtaining in the oil circulating systems of these paper machines necessitate the use of oils which are characterized by essentially inconsistent properties. For example, the oil must have sufficient emulsification properties to insure the pickup of any moisture in the system, particularly in the anti-friction bearings, and still be characterized by sufficient demulsification property to release the water content in the time the oil normally remains in the reservoir, i.e., normally about an hour or so. Such oils must have high load carrying capacity at high temperature and simultaneously be capable of acting as a bearing and gear coolant. The use of higher speeds in paper machines requires higher temperatures to effect drying in the shorter time available. Higher speeds and temperatures aggravate the lubrication problem as does the fact that shutdowns for bearing failures and the like result in losses of the order of thousands of dollars per hour.

We have now discovered a novel lubricating composition especially useful as a circulating system oil for paper machines. By our invention a lubricant is disclosed which provides rust protection, is oxidation resistant at high temperatures, is characterized by improved load carrying capacity and improved film strength, and is especially distinguished by a unique balance of emulsification and demulsification properties. This aspect relating to emulsification and demulsification properties characterizes the lubricant composition with the property of emulsifying moisture which normally enters the lubricating lines, the bearing and gearing housings, etc. and still permits ordinary demulsification of the

2

resulting emulsion, when the oil enters the settler-reservoir system, in the time the oil is normally resident in this part of the system, without the necessity of employing special techniques or demulsifiers to effect the demulsification.

Our invention thus is a lubricating composition consisting essentially of a calcium or barium mahogany petroleum sulfonate detergent, a metal dithiophosphate oxidation inhibitor, e.g. zinc dithiophosphate, a small amount of alkyl phenyl phosphate and a lubricating oil. In terms of concentrations, the components of our mixture are present in amounts within the following ranges:

	Weight percent
Lube oil	75 to 99
Sulfonate	0.3 to 20
Metal dithiophosphate	0.5 to 1.8
Alkyl phenyl phosphate	0.3 to 3.5

We have found it advantageous to include an anti-foam agent in our composition, such as a silicone polymer having a viscosity of 100 centistokes at 25° C. and known commercially as DCF (Dow Corning Fluid No. 200-100). The anti-foam agent, when employed, is present in amounts of about 0.0005 to 0.0015 weight percent. The preferred products of our invention have the following composition: about 93 to 98.5 percent oil, about 0.5 to 5 percent calcium or barium sulfonate, about 0.6 to 1.2 percent metal dithiophosphate, and about 0.5 to 1.0 percent alkyl phenyl phosphate.

Each of the components employed in our new composition is commercially available. For example, the lubricating oil employed is advantageously a mineral lubricating oil, and in general, can be a solvent refined or distilled neutral oil, solvent refined bright stock or the like or blends of two or more lubricating oil fractions, and can be derived from Mid-Continent, naphthenic or Pennsylvania crudes. An advantageous blend consists of about 24 volume percent of a solvent refined Mid-Continent neutral oil having a viscosity of about 200 SUS at 100° F. and about 76 volume percent of a solvent-refined Mid-Continent bright stock having a viscosity of about 120 SUS at 210° F.; this blend has a viscosity of about 975 SUS at 100° F. The amount and type of oil included is chosen so that the resulting composition has a viscosity of about 650 to 1000 SUS at 100° F., and preferably about 650 to 850 SUS at 100° F. Also, the base lubricating oil is chosen so that the compositions have a viscosity index of at least about 85 and preferably at least about 95 in order to enhance their demulsification properties.

The calcium or barium mahogany petroleum sulfonates employed in our composition are those obtained by neutralizing the oil-soluble petroleum sulfonic acids obtained as in conventional treatment of liquid petroleum oil fractions with oleum to produce medicinal and other highly refined oils. More particularly, a gas oil or lube oil fraction is contacted with oleum, sulfur trioxide or other sulfonating agent, the resulting sludge layer is separated and the mahogany sulfonic acids contained in the oil layer are neutralized with lime or barium oxide, as appropriate, in water. These sulfonates can be produced by various methods to provide normal

or basic sulfonates. When the sulfonate is basic we prefer that at least about 1.1 times the amount of calcium or at least about 1.5 times the amount of barium, as appropriate, be present than is needed to provide a neutral or normal sulfonate. A carbonated sulfonate which can be employed can be obtained by contacting the mahogany sulfonate, e.g. a basic barium sulfonate, with carbon dioxide until the strong basicity of the sulfonate to phenolphthalein is reduced and a final pH of about 7 to 8.5 is obtained. This can be carried out, for example, by introducing the sulfonate to the top of a packed column and then feeding carbon dioxide to the bottom of the tower. The carbonated mahogany sulfonate is then recovered and vacuum dried to obtain the final product. As an example, a typical carbonated basic barium sulfonate prepared from an oleum-treated West Texas gas oil fraction analyzed 2.86 percent barium and had a base No. to pH 4 of 11.3. The sulfonate usually contains unreacted lubricating oil which can be added to our compositions as part of the base oil.

The metal dithiophosphate oxidation inhibitors, such as zinc dithiophosphate, and the alkyl phenyl phosphate components of the new compositions are also well known. In general the metal dithiophosphates to be employed are diesters and contain about 3 to 18 carbon atoms in the organic radicals and preferably 3 to 10 carbon atoms. Metal dithiophosphates can be made by any known procedure, for example by contacting the reaction product of a suitable alcohol and phosphorus pentasulfide with a metal oxide, e.g. zinc oxide. Alkyl phenyl phosphates employed contain one or two alkyl groups per molecule with each alkyl chain having about 3 to 18 carbon atoms, and preferably 3 to 10 carbon atoms; in the dialkyl forms, the alkyl radicals need not be the same. Mixtures containing monoalkyl and dialkyl phenyl phosphates can also be employed. Alkyl phenyl phosphate, dialkyl phenyl phosphates or mixtures of monoalkyl and dialkyl phenyl phosphates are prepared typically by reacting phosphorus pentaoxide with a commercial grade phenol, e.g. diamyl phenol, at an elevated temperature on the order of 275° F. Typical examples of satisfactory phosphates include mono- and dibutyl phenyl phosphate, dipropyl phenyl phosphate, hexyl phenyl phosphate, dihexyl phenyl phosphate, pentyl hexyl phenyl phosphate, etc. The alkyl phenyl phosphate and metal dithiophosphate can also be obtained in solution in lubricating oil which can be added as part of the base oil of our compositions.

Compositions of the present invention can be made without observing special conditions of temperature, pressure, order of mixing or the like. For example, each of the components may be added to the oil base separately, or the zinc dithiophosphate, alkyl phenyl phosphate and sulfonate can be premixed in the desired proportions and then added to the oil base. As a practical matter we prefer to heat the resulting mixture to about 100° F. to facilitate rapid solution and stir the mass to insure a homogeneous mixture.

The invention will be described further with reference to the following specific examples:

EXAMPLE I

A composition was made by adding 1.4 pounds of zinc dithiophosphate, obtained by reacting zinc oxide with the reaction product of P_2S_5 and a mixture of hexanol and heptanol, 1.0 pound of diamyl phenyl phosphate and 15 pounds of barium mahogany petroleum sulfonates to 82.6 pounds of a mineral oil blend composed of 24 volume percent of a solvent-refined Mid-Continent neutral oil having a viscosity of 200 SUS at 100° F. and 76 volume percent of a solvent refined Mid-Continent bright stock having a viscosity of 120 SUS at 210° F. The resulting compositions had the following characteristics:

Table I

Gravity	26.9
Flash, °F.	445
Fire, °F.	505
5 Viscosity at 100° F.	780
Viscosity at 130° F.	332
Viscosity at 210° F.	77.8
Viscosity index	96.0
Pour, °F.	10
10 Color	7
Carbon residue, percent	1.41
Sulfated ash, percent	1.05
Acid No. D-974	1.18
Acid No., D-664	1.41
15 Base No., D-664	1.30
Barium, percent	0.511
Phosphorus, percent	0.118
Zinc, percent	0.082
Sulfur, percent	0.40
20 Foam, ASTM D-892:	
Sequence I	95-0-3'6"
Sequence II	160-0-3'40"
Sequence III	60-0-2'36"

25 The composition of this example was subjected to various tests to determine its usefulness as a paper machine circulating system oil. For purposes of comparison, tests also were conducted on four commercially available paper machine circulating system oils. The data obtained are:

	Composition Of Example	Commercial Oils			
		A	B	C	D
35 Steam Emulsion Test:					
Percent Oil recovered in 3 min.				100	
Percent Oil recovered in 20 min.	85-95	20-65	5-15		0-15
40 Modified Navy Emulsion Test:					
Percent Oil recovered in 19 min.	100				
Percent Oil recovered in 60 min.		85	10	15	80
Humidity Cabinet.	Pass	Pass	Fail	Fail	Fail
Hours.	200	200	24	72	96
45 Timken Load Carrying Capacity:					
Lbs. Pass	25	17	16	16	20
Lbs. Fail	28	20	19	19	23

The steam emulsion test gave somewhat erratic results on our composition, and on commercial oils A, B and D. The Navy emulsion test, however, gave reasonably reproducible results for all the oils tested. The decided superiority of our oil is clearly shown in this test. The results of the humidity cabinet and load carrying capacity tests are further indicative of the superior properties of our compositions.

The following tables, Table II and Table III, include additional data showing the advantageous properties of our compositions.

Table II

Composition	Weight Percent	
	(1)	(2)
65 Base Oil	Balance	Balance
Zinc Dithiophosphate of Example I	0.84	0.84
Diamyl Phenyl Phosphate	0.3	1.8
Barium Mahogany Petroleum Sulfonate (Base No. 127, Wt. Percent Ba 34.9)	.15	1.5
70 DCF	0.001	0.001
Viscosity Index	96.8	97.0
Viscosity, SUS at 100° F.	775	802
Tests:		
Modified Navy Emulsion Test, Minutes for 100% Recovery of oil	38	34
Humidity Cabinet	Pass	Not Run
Hours	200	

The base oil of the above compositions was comprised of a blend as defined in Example I and small amounts of lubricating oil employed as diluent for the additives. The zinc dithiophosphate and diamyl phenyl phosphate were added as approximately 60 percent concentrates while the sulfonate was about 13 percent active.

Table III

Composition	Weight Percent			
	(a)	(b)	(c)	(d)
Base Oil.....	Balance	Balance	Balance	Balance
Basic Barium Mahogany sulfonate Oil Concentrate, About 10% Active Ingredient (Base No. 14.3, Wt. Percent Ba 3.54).....	15.0			
Carbonated Basic Barium Mahogany Sulfonate Oil Concentrate, About 13% Active Ingredient (pH 7.1, Wt. Percent Ba 4.54).....		11.6		
Basic Calcium Mahogany Sulfonate Oil Concentrate About 10% Active Ingredient (Base No. 4.4, Wt. Percent Ca 0.61).....			15	25.8
Zinc Dithiophosphate (of Example I) Oil Concentrate About 60% Active Ingredient.....	1.4			
Zinc Dithiophosphate (of Example I) Oil Concentrate About 47% Active Ingredient.....		1.8	1.8	1.8
Diamyl Phenyl Phosphate Oil Concentrate About 60% Active Ingredient.....		1.0	1.0	1.0
DCF.....	0.001	0.001	0.001	0.001
Viscosity Index.....	98.3	97.7	96.4	101.8
Viscosity, SUS at 100° F.....	814	654	725	650
Tests:				
Modified Navy Emulsion Test at 180° F.—				
Minutes for 100% Recovery of Oil.....		26	24	30
Percent Oil Recovered in 60 Minutes.....	85			

The base oil of composition (a) was comprised of a blend as defined in Example I, and in addition the small amounts of lubricating oil employed as diluent for the additives were also in the composition. The base oil of compositions (b), (c) and (d) was comprised of a mineral oil blend composed of 29 volume percent of a solvent-refined Mid-Continent neutral oil having a viscosity of 200 SUS at 100° F. and 71 volume percent of a solvent-refined Mid-Continent bright stock having a viscosity of 120 SUS at 210° F. The compositions also contained the lubricating oil present in the additives. A comparison of the data presented on composition (a) and the data presented for the composition prepared in Example I on page 7, lines 24 to 26, for example, also illustrate the necessity of employing the alkyl phenyl phosphate along with the sulfonate to obtain adequate emulsifying and demulsifying action since upon subjection of composition (a), which does not contain diamyl phenyl phosphate, to the modified Navy emulsion test at 180° F., sixty minutes were required to recover 85 percent of the oil whereas upon subjection of the composition prepared in Example I, which does contain diamyl phenyl phosphate, only nineteen minutes were required to recover all of the oil.

This application is a continuation-in-part of application Serial Nos. 473,463, filed December 6, 1954, and 573,085, filed March 22, 1956, both now abandoned.

We claim:

1. A lubricant composition consisting essentially of about 75 to 99 weight percent of a mineral lubricating oil, about 0.3 to 5 weight percent of a sulfonate selected from the group consisting of calcium mahogany petroleum sulfonates and barium mahogany petroleum sulfonates, about 0.5 to 1.8 weight percent of zinc dialkyl dithiophosphate containing about 3 to 18 carbon atoms in the organic radicals and about 0.3 to 3.5 weight percent of alkyl phenyl phosphate in which each alkyl chain present contains about 3 to 18 carbon atoms, said composition having a viscosity index of at least about 85 and a viscosity (SUS) at 100° F. of about 650 to 1000.

2. The composition of claim 1 in which the zinc dialkyl dithiophosphate containing about 3 to 10 carbon atoms in the organic radicals and, the alkyl phenyl phosphate

in which each alkyl chain present contains about 3 to 10 carbon atoms.

3. A lubricant composition consisting essentially of about 75 to 99 weight percent of a mineral lubricating oil, about 0.3 to 5 weight percent of a calcium mahogany petroleum sulfonate, about 0.5 to 1.8 weight percent of

zinc dialkyl dithiophosphate containing about 3 to 18 carbon atoms in the organic radicals and about 0.3 to 3.5 weight percent of alkyl phenyl phosphate in which each alkyl chain present contains about 3 to 18 carbon atoms, said composition having a viscosity index of at least about 85 and a viscosity (SUS) at 100° F. of about 650 to 1000.

4. The composition of claim 3 wherein the sulfonate is a carbonated basic sulfonate.

5. The composition of claim 4 wherein the alkyl phenyl phosphate is diamyl phenyl phosphate.

6. The composition of claim 4 wherein the composition has a viscosity index of at least about 95.

7. The composition of claim 4 wherein the alkyl phenyl phosphate is diamyl phenyl phosphate and the composition has a viscosity index of at least about 95.

8. A lubricant composition consisting essentially of about 75 to 99 weight percent of a mineral lubricating oil, about 0.3 to 5 weight percent of barium mahogany petroleum sulfonate, about 0.5 to 1.8 weight percent of zinc dialkyl dithiophosphate containing about 3 to 18 carbon atoms in the organic radicals and about 0.3 to 3.5 weight percent of alkyl phenyl phosphate in which each alkyl chain present contains about 3 to 18 carbon atoms, said composition having a viscosity index of at least about 85 and a viscosity (SUS) at 100° F. of about 650 to 1000.

9. The composition of claim 8 wherein the sulfonate is carbonated.

10. The lubricant composition of claim 8 wherein the alkyl phenyl phosphate is diamyl phenyl phosphate.

11. The lubricant composition of claim 8 wherein the composition has a viscosity index of at least about 95.

12. The lubricant composition of claim 8 wherein the alkyl phenyl phosphate is diamyl phenyl phosphate and the composition has a viscosity index of at least about 95.

References Cited in the file of this patent

UNITED STATES PATENTS

2,340,331	Knutson et al.	Feb. 1, 1944
2,369,632	Cook et al.	Feb. 13, 1945
2,418,422	Palmer	Apr. 1, 1947
2,638,447	Otto et al.	May 12, 1953
2,698,835	Otto	Jan. 4, 1955