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METHOD AND COMPOSITION FOR LUBRICATING UNDER WET CONDITIONS

Harold J. Watson, Danville, Va., and Raymond B. Tierney, Wappingers Falls, N.Y., assignors to Texaco Inc., a corporation of Delaware

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This invention relates to a method and composition for lubricating modern machinery under wet conditions and particularly to a paper making machine employing a lubricating oil circulating system.

This is a continuation-in-part of application Serial No. 658,021, filed May 9, 1957, now abandoned.

The dryer section of a modern Fourdrinier paper making machine consists of as many as one hundred steam heated dryer rolls weighing many tons and employing heavy journal and double roller self-aligning bearings which carry the dryer rolls at speeds as high as 150 r.p.m. The rolls are geared together at their journals in order to synchronize their running. In addition to the paper dryers in the dryer section there are similar rolls for drying the felt used in the drying process and a greater number of small idler rolls over which the felt is threaded in the drying operation. These smaller rolls also employ roller bearings and synchronizing gears necessary for their proper operation.

In order to provide proper and adequate lubrication for the bearings and gears in this high speed, high pressure machinery, lubricating oil circulating systems were found to be necessary. Where so many costly bearings and gears are involved, the circulating oil system provides adequate lubrication and also removes considerable heat, which is very desirable.

The possibility of oil contamination by water in the circulating system on a dryer section is always present. The water enters the oil either by condensation of the steam in the cooler parts of the circulating system or by leaks which frequently develop in the steam joints. Water contamination is a considerably more serious problem in these modern high speed machines since they are lubricated with relatively water-sensitive detergent type oils in comparison to the straight mineral oils previously used and from which the water readily separated. It has been necessary in order to ensure relatively trouble-free operation to exercise every precaution to keep water out of the circulating oil system. However, despite such precautions, oil contamination with water is prevalent in paper machine operation.

The metal sulfonates which were used to obtain the detergency desirable in prior paper machine lubricants also increased the emulsification tendency of the mineral oil. When the water-oil emulsion was formed during the circulation of the oil composition, the lubricating function of the mineral oil was seriously curtailed. The oil, with the emulsifying agency of the detergent sulfonates, did not separate from the water sufficiently before it was recirculated, thus greatly reducing its effectiveness. Furthermore, prior to the present invention, water which entered the lubricating oil composition soon leached additives placed in the oil for detergency, additional oxidation and corrosion protection, and improvement of the extreme pressure property of the oil.

Another lubricating problem occurring in paper machine operation is oil oxidation. Bearings and gears are influenced by the steam which is used in the dryer section. For example, steam at pressures of about 125 p.s.i. and having a temperature of approximately 350° F. is frequently encountered in present operations, and bearing temperatures are estimated to be frequently over 275° F.

The effect of increased steam pressures on lubrication has been to require a more oxidation-resistant oil and one with sufficient load-carrying capacity at the higher temperatures to protect the bearings from failure. The comparatively high contact pressures which must be maintained between the surfaces of the couch rolls and the calender rolls of the paper machine in order to develop the necessary squeezing are of necessity imparted to the bearings which carry these rolls. This fact necessitates further consideration of the load-carrying ability of the oil. Thus the base oil should be fortified with an antioxidant and extreme pressure additive to obtain proper lubrication of the paper machine.

Corrosion protection of the metal parts of the machinery to be lubricated is also a necessity because of the water present in the system. Additives functioning as corrosion inhibitors are generally incorporated in circulating lubricants exposed to excessively moist conditions, for protection in this respect.

The problem, therefore, which is solved by the present invention, is the adequate lubrication of a paper machine wherein the lubricant composition is exposed to water contamination. Thus in accordance with this invention, the method of lubricating a paper machine comprises circulating an oil composition through the bearings and gears of said machine consisting essentially of a mineral lubricating base oil having an SUS viscosity at 100° F. of from 50 to 2500, and containing a detergent selected from the group consisting of alkaline earth metal, magnesium, zinc, and amine salts of dinonylnaphthalene sulfonic acid wherein the nonyl groups are highly branched, periodically removing that portion of water from the system which separates from the oil composition and then recirculating said composition through the bearings and gears of said machine.

The method of the invention also includes utilizing a circulating lubricant composition having an antioxidant additive in combination with the dinonylnaphthalene sulfonic acid salt incorporated therein to improve the performance of the composition in use. The preferred additional additive or additive combination is one which functions as an oxidation and corrosion inhibitor to prevent deterioration of the mineral oil composition in service while protecting metal parts from corrosion. Other useful additives include extreme pressure additives, pour point depressants, etc.

The invention also includes a novel circulating oil composition for lubricating the dryer sections of paper machinery and other machinery requiring lubrication under similar conditions in which fast separation from water is desirable. The novel composition comprises a mineral lubricating base oil having an SUS viscosity at 100° F. of from 50 to 2500, a compound selected from the group consisting of alkaline earth metal, magnesium, zinc, and amine salts of dinonylnaphthalene sulfonic acid, wherein the nonyl groups are highly branched, in an amount ranging from 0.1 to 4 percent by weight of the composition; and a metal dialkyl dithiophosphate in an amount ranging from 0.1 to 3.0 percent by weight based on the composition. Very advantageously, the dinonylnaphthalene sulfonic acid salt is present in the composition in an amount from about 0.5 to 2 percent by weight, and the metal dialkyl dithiophosphate is present in an amount from about 0.1 to 2 percent, preferably from about 0.5 to 1 percent by weight of the composition. The composition preferably also includes from about 0.05 to 1.0 percent of a chlorinated paraffin wax-naphthalene condensation product to reduce pour point, and a foam inhibitor, such as a 10 percent solution of dimethyl silicone polymer in kerosene in the amount of about 100 to 300 p.p.m.

The salts of dinonylnaphthalene sulfonic acid applicable to the present invention and the method of their preparation are set forth in U.S. 2,764,548 to King et al., issued September 25, 1956. Briefly, these compounds are prepared by dissolving dinonylnaphthalene in an organic solvent which is substantially unreactive with sulfuric acid. This solution is treated with sulfuric acid to form the monosulfonic acid. After the reaction a carrier oil is added to the product to facilitate handling. The dinonylnaphthalene is initially produced by replacing some of the hydrogen atoms on the naphthalene nucleus by highly branched nonyl groups. This is brought about by alkylating the naphthalene with highly branched nonenes, for example, tripropylene with a suitable alkylation catalyst. The King et al. patent further discloses that the salts are formed by neutralizing the acid with an equivalent amount of metal or amine. The preferred salts are those derived from the alkaline earth metals. The range of the amount of this compound in the composition is from 0.1 to 4 percent by weight but the preferred amount is about 1.0 percent by weight (active ingredient) basis performance.

Examples of other additives useful in this invention which are used in combination with the dinonylnaphthalene sulfonates include a metal dialkyl dithiophosphate having alkyl groups containing from 1 to 30 carbon atoms which acts simultaneously as a corrosion inhibitor, antioxidant and extreme pressure agent for the base oil. Dithiophosphate metal salts, particularly calcium and zinc salts, are produced by the reaction of metal hydroxide, oxide or metal, per se, with alkyl dithiophosphates resulting from the reaction of monohydroxy alcohols with phosphorus pentasulfide. Preferred alcohols for reaction with P_2S_5 are methyl isobutyl carbinol, isopropyl alcohol, lauryl alcohol, cyclohexanol, methyl cyclohexanol, and capryl alcohol.

Other oxidation inhibitors which are useful are the hindered phenols such as 2,6-di-t-butyl-4-methylphenol and alkylated diphenylamines.

Extreme pressure additives include chlorinated paraffins, sulfurized oils, phosphorus compounds, etc.

Corrosion inhibitors include olefin-P_2S_5 products, sulfurized wax, mercaptobenzothiazole, metal dialkyldithiocarbamates, dibasic carboxylic acids, and nono- and dialkyl phosphoric acids.

The pour depressant found to be very useful in the composition is an alkylated aromatic type compound. Compounds of this type are, for example, prepared by condensing an aliphatic compound having a long aliphatic hydrocarbon chain such as chlorinated paraffin wax or olefins corresponding thereto, with an aromatic compound such as naththalene, phenol, benzene, biphenyl, etc. The preferred product is obtained by condensing about 100 parts by weight of chlorinated paraffin wax having a chlorine content of about 10 to 15 percent with about 10 to 20 parts by weight naphthalene in the presence of aluminum chloride catalyst. Similar type pour point depressor compounds can be prepared and used in the lubricant composition. These are the Friedel-Crafts condensation products of low molecular weight alcohols (having less than 10 carbon atoms) and aromatic compounds.

Many detergent additives were bench tested to determine whether their water-separating properties in a lubricating oil would permit their use in a paper machine oil. The following table shows some of the results of the emulsion test at 180° F. (Fed. Method 791–3201.5). In each case the detergent was added in the amount of about 1 percent (active ingredient) to the base oil, consisting of a mixture of about one-third paraffin distillate and two-thirds paraffin residual oil having a gravity ° API of 26.7, an SUS viscosity at 100° F. of 658, a pour point of —10° F. and a viscosity index of 83.1, about 0.1 percent by weight of a chlorinated paraffin wax-naphthalene condensation product and 150 p.p.m. (added) of a 10 percent solution of dimethyl silicone polymer in kerosine.

TABLE I

Emulsion test at 180° F.

Run	Detergent	H_2O Separation at 60 min., cc.
1	None	40 (45 min.).
2	Neutral barium dinonylnaphthalene sulfonate	40 (5 min.)
3	Sodium sulfonate (petroleum)	36
4	do	36
5	do	28
6	Sodium sulfonate (synthetic)	30
7	do	36
8	Neutral calcium sulfonate (petroleum)	2
9	do	39
10	Neutral barium sulfonate (di-wax benzene)	10
11	Basic calcium sulfonate (petroleum)	10
12	Basic barium sulfonate (di-wax benzene)	30
13	Basic barium sulfonate (petroleum)	30
14	Calcium phenolate sulfide	0
15	do	0

The above table shows representative detergent compounds tested. None of these detergents demonstrated the excellent water-separating properties that the salt of the dinonylnaphthalene sulfonic acid lent to the base oil. This sulfonate, surprisingly, is the only detergent found which improved the water separating properties of the blends containing it, as seen in runs 1 and 2.

The process and lubricant composition of the invention were evaluated in a bench test developed to simulate the sequence of events through which the circulating oil is put during the paper drying operation. This sequence can be depicted as follows:

(1) As the oil is passed through the system it is quickly contaminated by water and is very shortly saturated therewith. The excess water is separated out in the settling portion of an oil reconditioning apparatus incorporated in the circulating system. However, the oil remains saturated with water.

(2) If any of the additives in the mineral oil are sensitive to water or are capable of being leached by water, this action will occur from the very beginning and before a measurable oxidation occurs. This sensitivity or leaching action would be greatly accelerated in machines showing high water contamination.

(3) Very slowly, oxidation of the oil takes place with accompanying degradation of the lubricant composition. Deposits and gel formation begin to build up in the filtering portion of the oil reconditioning system. The filtering medium is generally a cellulose fabric, such as cotton fiber which is subject to deterioration in contact with aqueous solutions of acidic decomposition products of the additives. Active clay-type filters cannot be used in this service since they selectively adsorb the additives from the oil and lower their effectiveness.

The paper machine oil bench test to which the oil composition of the invention was subjected consisted of thoroughly water washing the test oil with an equal volume of water. After repeating this water washing step a second time, the water-washed oil was then subjected to oxidation at 200° F. in the presence of iron and copper, with 2 (wt.) percent water added daily. One liter of air per minute was bubbled through the oil-water mixture. Strips of filter bag material were added at the beginning of the test to the test oil in order to determine the extent of deterioration caused by the test oil. The actual test conditions were as follows: 2 liters of test oil were washed at 200° F. with 2 liters of water. The same wash was repeated. Then 1600 g. of test oil, 32 ml. of water, ASTM iron (steel) and copper strip oxidation catalyst (as described in ASTM Test D943–53T) and two 2 x 6 in. cotton fiber-containing filter cloth strips were heated at 190 to 200° F. in a flask equipped with a condenser while 1 liter of air per minute was bubbled therethrough. 32 ml. of water (2 percent) was added daily. Water from the bottom of the flask was removed weekly (except after 168 hours).

Two paper machine circulating oil compositions were

tested for character changes while being subjected to the above procedure. The composition of the invention consisted of a mineral lubricating base oil, which was a mixture of about one-third paraffin distillate and two-thirds paraffin residual oil, having a gravity ° API of 26.5, a viscosity SUS at 100° F. of 653, a pour point of −10° F. and a viscosity index of 85, 2.0 (wt.) percent of a 50 percent concentrate of barium dinonylnaphthalene sulfonate in a light mineral oil, 0.75 (wt.) percent of zinc dimethylisobutyl carbinyl dithiophosphate, 0.10 (wt.) percent of a chlorinated paraffin wax-naphthalene condensation product, and 150 p.p.m. (added) of a 10 percent solution of dimethyl silicone polymer in kerosene. This composition, for convenience, will hereinafter be designated "lubricant A."

The composition used for comparison was one showing relatively good results in the field prior to this invention and consisted of about the same base oil as mentioned above for "lubricant A," about 2.0 (wt.) percent of a 50 percent concentrate of a neutral calcium petroleum sulfonate in a light mineral oil, about 0.5 (wt.) percent of calcium alkyl phenolate, about 0.75 (wt.) percent of zinc di-methylisobutyl carbinyl dithiophosphate, about 0.05 (wt.) percent of a chlorinated paraffin wax-naphthalene condensation product, and 150 p.p.m. (added) of a 10 percent solution of dimethyl silicone polymer in kerosene. This composition will hereinafter be referred to as "lubricant B." The results obtained by periodic testing while the lubricants were subjected to the oxidation conditions simulating actual paper machine operation are given in the following tables.

Table II presents data establishing superior additive retention by the lubricant of the invention.

TABLE II

Determination of additive metals in used oil samples

Hours	Lubricant A			Lubricant B		
	Percent Ba	Percent Zn	Percent P	Percent Ca	Percent Zn	Percent P
0	0.11	0.071	0.060	0.041	0.078	0.031
after water wash	0.12	0.07	0.053	0.022	0.069	0.032
504	0.071	0.040	0.051	0.0028	0.012	0.026
1,008	0.023	0.041	0.042	0.0008	0.003	0.018

The above table shows much greater additive retention by "lubricant A," the composition of the invention, basis additive metal analysis. The additives in "lubricant A," therefore, will continue to perform much longer in the intended manner.

The corrosion tendencies of the oils on copper and iron (steel) are shown in the following table.

TABLE III

Visual observation of copper and iron strips

Metal	504 Hours		1,008 Hours	
	Lubricant A	Lubricant B	Lubricant A	Lubricant B
Copper	Black stain	Black stain	Black stain, trace removed at bottom.	Most of surface etched. Remainder black, flaking deposit.
Iron	Clean, except for slight stain at bottom.	Pitted, no stain	Clean, except for 25% smooth black stain on bottom, no pitting.	Deeply pitted, rusted. Black deposit.

Obviously, the corrosion resistance of "lubricant A," is much superior to "lubricant B" as observed from the condition of the copper and iron (steel) strips at the termination of the test procedure. The lack of pitting on the iron (steel) strips in "lubricant A" is extremely significant since pitting on bearing surfaces is known to be a chief cause of bearing failures.

In addition to the above evidence of corrosion resistance by "lubricant A" as compared to "lubricant B," the following table shows the visual observations made of the water layer which was separated from the oil compositions after 504 hours and after 1008 hours.

TABLE IV

Visual observations of water layer

	504 hours	1,008 hours
Lubricant A	Colorless	Yellow.
Lubricant B	Green	Greenish brown.

The above observation of green color in the water layer separated from "lubricant B" was indicative of a high amount of copper which suggested an attack of some kind on copper by "lubricant B." An analysis of the water layer separated from "lubricant B" showed 0.011 percent copper and 0.029 percent iron after 1008 hours whereas only 0.05 p.p.m. of copper and about 0.01 p.p.m. of iron were found in the water layer separated from "lubricant A."

The antiwear characteristics of the lubricant of the invention have been determined by means of the paper machine oil wear test performed on the Shell four-ball extreme pressure lubricant tester. In this test the SKF steel balls of 0.5 inch diameter are cleaned with Stoddard solvent and MEK, dried and locked in position in the test cup. A charge of 10 to 15 cc. of the test lubricant is then put into the test cup. A test run consists of at least 2-hour runs at 600 r.p.m., 300° F. and a 15 kg. load on the balls. The mean scar diameter on the three lower balls for each run is recorded. The value reported on a test consists of the average of the results of the two runs if they are within 0.020 mm. of each other. If they are not within this limit, a third run is made and the value reported is the average of these three runs. The following table gives the results of this test on "lubricant A" and "lubricant B," at various times during their exposure to the simulated service operation.

TABLE V

Paper machine oil wear test

Hours	Scar diameter, mm.	
	Lubricant A	Lubricant B
0	0.280	0.318
504	0.333	0.681
1,008	0.318	0.758

The extreme pressure and wear characteristics of "lubricant A" are definitely shown in the above table to be very superior to "lubricant B." This fact is further proof of the greater additive retention of the lubricant of the invention.

The excellent properties of the oil composition of the invention, "lubricant A," under extreme conditions as demonstrated in the foregoing tables prove that the additives which lend these properties to the oil are not readily leached by high water contamination of the oil. As further evidence of this, the tensile strength of the

cotton fiber-containing filter bag strips which were placed in both oil compositions, was measured. The tensile strength, in relative units, of those strips in "lubricant A" was 63 after 504 hours and 7½ after 1008 hours while the tensile strength of the strips from "lubricant B" was 34 after 504 hours and 6 after 648 hours in the oil.

The slower process of oxidation and the excellent results obtained by "lubricant A" in this respect are demonstrated in the following tables.

TABLE VI

Neutralization number determination of oil composition

Hours	Lubricant A	Lubricant B
0	0.03	0.09
336	0.09	0.08 alk
504	0.04	0.13
840	0.08	0.89
1,008	0.53	1.07

It is quite evident from the above table that the Neut. No. rise of the lubricant of the invention is much slower that that of "lubricant B" which contains the prior art sulfonate as a detergent. This indicates much better protection against oxidation.

The following table shows further evidence of the excellent oxidation resistance of "lubricant A" as compared to "lubricant B" after 504 hours of exposure to the condition of the paper machine oil bench test.

TABLE VII

Visual observations of filtered samples

Observed Matter	504 Hours	
	Lubricant A	Lubricant B
Filtered Oil	Green bloom no oxidized odor.	Dark brown, oxidized odor.
Precipitate	Trace of yellow-brown sludge.	Considerable dark brown sludge.

The visual observations depicted in the above tables present further indication of the excellent oxidation stability of the lubricant of the invention under wet conditions. The "lubricant B" more readily darkened and developed an oxidized odor. The considerable dark deposits precipitated from the filtered "lubricant B" resembled the gel formation obtained from deteriorated bags in field operation. "Lubricant A" was superior in all cases in the testing for oxidation stability under these severely wet conditions.

The advantages of the method of lubricating a machine under wet oxidizing conditions, such as are met in the dryer section of a paper making machine, have been made obvious from the foregoing description. The use of the salt of dinonylnaphthalene sulfonic acid in place of the ordinary metal sulfonates which lend equal detergency to the base oil under dry conditions is manifest. The metal dinonylnaphthalene sulfonate does not promote water sensitivity nor does it act as an emulsifier. Instead, it lends water-separating properties to the base oil and gives good detergency without becoming leached or causing other additives in the composition to be leached. The method of lubricating a paper machine dryer section or other machinery under wet conditions utilizing a circulating oil comprising a mineral base oil with a detergent amount of a metal dinonylnaphthalene sulfonate in accordance with this invention is a tremendous improvement in the field of lubrication.

Obviously, many midifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method of lubricating a machine wherein the lubricant is exposed to water contamination which comprises circulating an oil composition through the bearings and gears of said machine consisting essentially of a mineral lubricating base oil, a detergent amount of a compound selected from the group consisting of alkaline earth metal, magnesium, zinc, and amine salts of dinonylnaphthalene sulfonic acid wherein the nonyl groups are highly branched, and an antioxidant compound in an amount sufficient to inhibit mineral oil oxidation, periodically removing that portion of water which readily separates from the oil composition, and then recirculating said composition through the bearings and gears of said machine.

2. A method of lubricating a machine wherein the lubricant is exposed to water contamination which comprises circulating an oil composition through the bearings and gears of said machine consisting essentially of a mineral lubricating base oil, a detergent amount of an alkaline earth metal dinonylnaphthalene sulfonate wherein the nonyl groups are highly branched, and an oil-soluble metal dialkyl dithiophosphate wherein the alkyl groups contain from 1 to 30 carbon atoms in an amount sufficient to inhibit oxidation of the composition, periodically removing that portion of water which readily separates from the oil composition, and then recirculating said composition through the bearings and gears of said machine.

3. A method of lubricating a machine wherein the lubricant is exposed to water contamination comprising circulating an oil composition through the bearings and gears of said machine consisting essentially of a mineral lubricating base oil, from 0.1 to 4 percent by weight of barium dinonylnaphthalene sulfonate wherein the nonyl groups are highly browned, and from 0.1 to 2 percent by weight of an oil-soluble zinc dialkyl dithiosphosphate wherein the alkyl groups contain from 1 to 30 carbon atoms, periodically removing that portion of water which readily separates from the oil composition, and then recirculating said composition through the bearings and gears of said machine.

4. A method of lubricating a machine wherein the lubricant is exposed to water contamination comprising circulating an oil composition through the bearings and gears of said machine consisting essentially of a mineral lubricating base oil having an SUS viscosity at 100° F. of from 50 to 2500, about 1 percent by weight of barium dinonylnaphthalene sulfonate wherein the nonyl groups are highly branched, about 0.5 to 1 percent by weight of zinc di-methylisobutyl carbinyl dithiophosphate, about 0.05 to 1 percent by weight of a chlorinated paraffin wax-naphthalene condensation product, and a foam inhibiting amount of a dimethyl silicone polymer, periodically removing that portion of water which readily separates from the oil composition, and then recirculating said composition through the bearings and gears of said machine.

5. A circulating oil composition for lubricating machinery under wet conditions which comprises a mineral base oil having an SUS viscosity at 100° F. of from 50 to 2500, barium dinonylnaphthalene sulfonate wherein the nonyl groups are highly branched, in an amount ranging from 0.1 to 4 percent by weight of the composition, and an oil-soluble zinc dialkyl dithiophosphate wherein the alkyl groups contain from 3 to 12 carbon atoms in an amount ranging from 0.1 to 3.0 weight percent based on the composition.

6. A circulating oil composition for lubricating machinery under wet conditions which comprises a mineral base oil having an SUS viscosity at 100° F. of from 50 to 2500, barium dinonylnaphthalene sulfonate wherein the nonyl groups are highly branched, in an amount rang-

ing fror 0.5 to 2 percent by weight of the composition, zinc di-methylisobutyl carbinyl dithiosphosphate in an amount ranging from 0.5 to 1 percent based on the composition, about 0.05–1.0 percent by weight of a chlorinated paraffin wax-naphthalene condensation product, and a foam inhibiting amount of a dimethyl silicone polymer.

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