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3,050,466

ROLL OIL CONTAINING A PHOSPHORUS ACID ESTER AND AN OIL-MISCIBLE DICARBOXYLIC ACID

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The present invention relates to a method of lubricating metal rolling mills and to an improved lubricant therefor. More particularly it relates to a lubricating composition comprising a mineral lubricating oil containing a phosphorus acid ester and an oil-miscible dicarboxylic acid.

This is a continuation-in-part of our copending application Serial No. 240,028, filed August 2, 1951, now abandoned.

Roll oils are employed in cold rolling processes for lubricating and cooling the metal and the rolls. Because of the high unit pressures employed in operations of this type, oils employed for this purpose must have good lubricity and film strength in order to avoid sticking and metal pickup, and in addition they must not cause slippage and loss of bite in mills of the type wherein the metal strip or sheet under only slight tension is passed between the rolls by means of the bite of the rolls upon the metal. When a metal product of high surface finish is desired it is necessary that the oil have good cooling properties in order to avoid heat staining of the metal, and in addition it is important that the oil should not form a stain upon the metal during the subsequent annealing process.

The lubrication requirements are particularly severe in the case of the Sendzimer mill, where the oil is required to have superior lubricating and cooling properties in addition to other special properties. The lubrication of the Sendzimer mill is unique in that one oil is usually employed both for bearing lubrication and as a roll oil; this places more stringent requirements on the oil used, but has the advantage of eliminating contamination difficulties. This mill is a high speed reversing mill of the cluster type used for the cold-rolling of metal strip to produce fine gauge strip of high surface finish. Force is transmitted by means of an hydraulic system through sets of anti-friction bearings to two small-diameter work rolls, between which the strip passes. Lubricant from a common source is supplied both to the surface of the work and to the bearings, and flows downwardly over the rolls into the lower part of the mill, where it is withdrawn and recirculated through cleaning and cooling means. An important function of the lubricant is the lubrication of the anti-friction bearings, so that it must have sufficient film strength to stand the load and also must have anti-wear properties for bearing life. However, slippage is an important problem in the operation of this mill, so that a limitation is thereby imposed upon the oiliness or lubricity of the lubricant employed. Superior heat conductance properties are necessary in this case to provide adequate cooling for the small-diameter work rolls. Oxidation stability and rust preventive properties are also required in order to protect the bearings and other mill parts in contact with the oil which is recirculated continuously for long periods of time, during which time it is repeatedly subjected to elevated temperatures at the roll bite.

When lubricating compositions of the types heretofore proposed as roll oils are employed in the Sendzimer mill, excessive bearing failures occur and other difficulties such as rusting of the mill parts, heat staining of the metal strip and oil "fogging," are encountered due to the in-

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sufficient lubricating and cooling properties of these compositions. Attempts to increase the lubricating properties of the oil sufficiently to decrease bearing wear by the use of higher viscosity oils or by additives have resulted in roll slippage and in decreased cooling properties of the composition. The choice of additives which may be employed in these oils is furthermore limited by the requirement that they must not cause staining of the metal strip during the annealing process.

In accordance with our invention an improved roll oil suitable for use in the Sendzimer mill comprises a mineral lubricating oil having incorporated therein about 0.5 to 3.0 percent by weight of tricresyl phosphate and at least about 0.001 percent by weight of an aliphatic dicarboxylic acid. The amount of tricresyl phosphate within the specified range is critical for obtaining the extreme pressure properties required without slippage and loss of bite of the rolls when the composition is employed for lubricating the Sendzimer mill. The preferred proportion range for the tricresyl phosphate is from about 1 to 2 percent by weight. The amount of aliphatic dicarboxylic acid employed will usually be from about 0.005 to 0.5 percent by weight, although larger amounts, up to about 3.0 percent by weight, may be employed if desired. Very advantageously, the composition also contains about 0.05 to 2.0 percent by weight, and preferably about 0.1 to 1.0 percent by weight, of an oxidation inhibitor of the phenolic type.

The mineral lubricating oil employed as the base oil is a medium to low viscosity oil from a paraffinic, naphthenic or mixed base crude. Lubricating compositions designed for use in rolling hard metals such as steel or steel alloys are preferably made from medium viscosity oils, suitably in the viscosity range of from about 90 to 110 seconds Saybolt Universal at 100° F. Lower viscosity oils, e.g. in the viscosity range from about 90 to about 50 seconds Saybolt Universal at 100° F., may be employed in lubricating compositions for use in rolling softer metals such as aluminum or brass.

Suitable aliphatic dicarboxylic acids are lower aliphatic dicarboxylic acids wherein the carboxy groups are separated by 1 to 4 carbon atoms, such as malonic, succinic, maleic, glutaric and adipic acids, having at least one aliphatic hydrocarbon substituent group containing from about 6 to 20 carbon atoms, preferably containing from about 8 to 16 carbon atoms. Such compounds are conveniently prepared as disclosed, for example, in U.S. 2,452,319, by condensing an unsaturated lower dicarboxylic acid anhydride, such as maleic acid anhydride, with a suitable olefin, and thereafter hydrolyzing to obtain the acid. Especially suitable olefins for this purpose are branched chain olefins obtained by the polymerization of C₃₋₄ olefins, or olefin mixtures comprising predominant proportions of branched chain olefins obtained by cracking petroleum fractions comprising large amounts of higher molecular weight branched chain hydrocarbons, such as petrolatum. In the acids thus produced there is an olefinic double bond, which may be present either in the medial alkylene group of the acid molecule or in the aliphatic substituent group. Thus the condensation product obtained from maleic acid anhydride may exist as an alkyl maleic acid, an alkenyl succinic acid, or mixtures thereof. For convenience, this product is referred to herein as alkenyl succinic acid without regard to the location of the unsaturated linkage. A hydrogenation may be carried out if desired to obtain a saturated product.

A particularly suitable aliphatic dicarboxylic acid for use in the lubricating compositions of this invention is obtained by condensing maleic acid anhydride with a propylene tetramer fraction, and thereafter hydrolyzing the condensation product. The process is very advanta-

geously carried out as described in copending application Serial No. 275,656, filed March 8, 1952, now U.S. 2,741,597, by thermally condensing maleic acid anhydride with propylene tetramer, boiling in about the range 350–480° F., purifying the condensation product by distillation followed by water washing, and finally converting it to the acid by heating it with water.

Phenolic oxidation inhibitors which may be employed in these compositions are alkylated phenols having sufficient alkyl carbon atoms to promote oil solubility. They are preferably tri-alkylated phenols having tertiary alkyl groups in the 2 and 6 positions, such as for example 2,4,6-tritertiary butyl phenol and 2,6-isopropyl-4-methyl phenol. A particularly effective compound of this type is 2,6-ditertiary butyl-4-methyl phenol, which is sold commercially under the trade name of "Paranox 441."

The following examples are given as illustrative of typical lubricating compositions suitable for use as roll oils which were compounded from the above materials in accordance with this invention.

4-methyl phenol was added as an oxidation inhibitor. This lubricant consisted of the following materials in substantially the following percentages by weight:

	Percent by weight
Tricresyl phosphate.....	1.500
Alkenyl succinic acid.....	0.015
Dilauryl ortho-phosphate.....	0.0025
Phenol	0.0005
2,6-ditertiary butyl-4-methyl phenol.....	0.300
Lubricating oil.....	Remainder

This product had an API gravity of 22.0, a flash point, COC, of 335° F., and a Saybolt Universal viscosity of 104.5 seconds at 100° F.

Lubricating properties of the above compositions indicative of their suitability for use as roll oils according to this invention were determined by suitable laboratory tests and the results are given in Table I below, in comparison with results obtained upon the base oil alone and upon the base oil containing 1.5 percent of tricresyl phosphate.

Table I

	Oil			
	Base oil	Base oil +1.5% tricresyl phosphate	No. 1	No. 2
Rusting: ASTM salt water rusting test (method D665-47T).....	Heavy rust.	Heavy rust.	Passes.....	Passes.
Load carrying:				
Almen value:				
Lbs.....	9.....	16.....	14.....	12.....
P.s.i.....	4,500.....	8,000.....	7,000.....	6,000.....
Navy four ball wear test, microns per minute.....	7.33.....	6.73.....	2.3.....	3.4.....
Falex wear test (3 hrs.; steel on steel; 150° F.; 10 lb. arm load) weight loss, mg.....	19.0, 22.5.....	3.6, 3.7.....	3.3, 3.1.....	9.2, 8.6.....
Oxidation corrosion:				
ASTM oxidation test (method D943-47T), hours to 2.0 neut., number.....	89.....	115.....	118.....	287.....
Corrosion and oxid. stab. test (method 630.8 of Fed. Spec. VV-L-791C) (72 hrs. at 250° F.):				
Metals weight change, mg./cm. ² :				
Steel.....		+0.03.....	-0.01.....	0.....
Aluminum.....		+0.06.....	0.....	0.....
Magnesium.....		+0.06.....	0.....	-0.01.....
Copper.....		+0.06.....	-0.02.....	-0.03.....
Cadmium.....		+0.03.....	+0.03.....	-0.03.....
Metal appearance.....		Copper dull.....	Copper slight peacock.....	Clean.....
Neut. number increase of oil.....		0.48.....	0.35.....	0.26.....
Kinematic viscosity increase of oil at 100° F., percent.....		8.....	7.....	6.....

EXAMPLE I

A lubricating composition was prepared by adding 1.500 percent by weight of tricresyl phosphate and 0.015 percent by weight of an alkenyl succinic acid to a naphthenic lubricating oil having an API gravity of 22.4, a flash point, COC, of 320° F., and a viscosity of 104.3 seconds Saybolt Universal at 100° F. The alkenyl succinic acid was a commercial product prepared by condensing maleic acid anhydride with a C₁₀₋₁₂ olefin fraction obtained by the thermal cracking of petrolatum, and thereafter hydrolyzing the condensation product by heating it with water. It was employed in the form of a commercial mixture containing about 45 percent of a low viscosity mineral lubricating oil, about 8 percent of dilauryl ortho-phosphate and about 1.5 percent of phenol. The lubricating composition thus obtained comprised the above materials in substantially the following amounts:

	Percent by weight
Tricresyl phosphate.....	1.500
Alkenyl succinic acid.....	0.0150
Dilauryl ortho-phosphate.....	0.0025
Phenol	0.0005
Lubricating oil.....	Remainder

The above product had an API gravity of 22.0, a flash point, COC, of 330° and a Saybolt Universal viscosity of 104.7 seconds at 100° F.

EXAMPLE II

Another lubricant was prepared of the same composition as that of Example I except that 2,6-ditertiary butyl-

The salt water rusting test of the foregoing table is an ASTM test (ASTM Designation D665-47T) employed to determine the anti-rusting characteristics of an oil under severe rusting conditions. For the present purposes, the oils were considered to have passed this test if no more than a few specks of rust were found upon the steel specimens after 48 hours.

The Navy four ball test is a laboratory test for determining the anti-wear properties of a lubricant. The test machine comprises a system of four steel balls, three of which are in contact with each other in one plane in a fixed, triangular position in a reservoir containing the oil sample, and a fourth ball above and in contact with the other three. In carrying out the test, the upper ball is rotated while it is pressed against the lower three at any desired pressure by means of a suitable weight applied to a lever arm, and the diameters of the scars on the three lower balls are measured by means of a low power microscope. The average diameter, measured in two directions on each of the three lower balls, is taken as a measure of the anti-wear characteristics of the lubricant. The results given in Table I were obtained as the average of 4 runs of 10, 40, 70 and 100 minutes' duration, employing new ½ inch steel first grade SKF balls for each run. The tests were conducted at room temperature at a speed of 1800 r.p.m. and under a 61.73 pound load.

The Almen test is a well known test used to compare and evaluate the "film strength" or extreme pressure characteristics of fluid lubricants. The test machine comprises a soft steel journal and a bearing consisting of 2 cold-

rolled steel half bushings so arranged that variable loads may be placed on the journal while the latter is run at 600 r.p.m. in a bath of the lubricant under test at room temperature. The load is increased gradually during the test up to the point of seizure, and the load carrying capacity of the oil expressed in terms of the weight at which seizure occurs and also in pounds per square inch.

The Falex wear test is also a laboratory procedure used to evaluate the wear characteristics of gear lubricants. The test machine comprises a steel test pin held in a bearing formed by two steel V-blocks which fit into a special jaw arrangement provided with lever arms and a hydraulic loading device for applying a constant load to the bearings. In carrying out the test, the test specimen, consisting of the pin and V-blocks, is immersed in a sample of the test oil maintained at the desired temperature, a load applied to the bearing, and the pin rotated at 290 r.p.m. for the period of the test. The pin and V-blocks forming the test specimen are weighed both before and after the test, and the amount of wear determined by the loss in weight of the test specimen. The data given in Table I were obtained by carrying out this test for 3 hours at 150° F. employing a 10 pound arm load.

The corrosion and oxidation stability test of the foregoing table was carried out according to method 530.8 of Federal Specification VV-L-791C (May 1945), modified by reducing the time from 168 hours to 72 hours.

As shown by the data given in Table I, lubricants of very superior lubricating and rust protective properties were obtained by means of the additives of our invention in a medium viscosity mineral lubricating oil. By addition of small amounts of phosphate ester and dicarboxylic acid in the range contemplated by our invention a lubricant having extreme pressure and anti-wear properties suitable for use as a bearing lubricant, as well as good rust protective properties were obtained. By the addition further of a small amount of 2,6-ditertiary butyl-4-methyl phenol, good oxidation resistance was also imparted to the composition.

Oil No. 2 was employed very successfully for several months as a roll oil for cold-rolling narrow gauge steel strip in a Sendzimer mill, operating with a strip rate of about 250 feet per minute while taking an 18-20 percent reduction. No bearing failures, slippage, rusting, staining of the metal strip, or other difficulties of any kind were encountered during this period due to deficient or unsatisfactory lubricating or cooling properties of this oil. When the base oil alone was employed for this purpose, excessive bearing failures resulted and also, because of insufficient cooling properties of the oil, heat staining of the metal strip and oil "fogging" occurred and the rolls turned black due to tempering. Rusting of the mill parts was also found, and more frequent changing of the oil was necessary because of the development of an objectionable degree of corrosiveness due to oxidation. With this oil containing 1.5 percent of tricresyl phosphate as the only additive, improved bearing lubrication and cooling were obtained, but the rust-preventive and oxidation resistance properties of the compositions were still unsatisfactory and a slight staining of the metal strip occurred during the annealing process.

Another lubricant of the same composition as oil No. 2 above except that it contained a different alkenyl succinic acid, has been employed extensively with very good results in commercial cold rolling operations. The alkenyl succinic acid employed in this lubricant was obtained by

the method which involves condensing maleic acid anhydride with propylene tetramer, as described in the said copending application Serial No. 275,656, now U.S. 2,741,597.

While the above examples may be regarded as the preferred compositions of this invention, it is to be understood that compositions coming within the purview of this invention may also be obtained by use of other dicarboxylic acids as described above, and employing different mineral oils, such as paraffinic oils and oils of lower viscosity. Different phenolic oxidation inhibitors may be employed also, particularly other alkylated phenols having tertiary alkyl groups in the 2 and 6 positions.

Obviously many modifications 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 roll oil for use in the cold rolling of metals consisting essentially of a mineral lubricating oil of about 50-110 seconds Saybolt Universal viscosity at 100° F. containing about 1.5 percent by weight of tricresyl phosphate and about 0.015 percent by weight of an aliphatic dicarboxylic acid wherein the carboxy groups are separated by 1-4 carbon atoms and having a C₆₋₂₀ aliphatic hydrocarbon substituent group, the said roll oil being substantially non-staining to steel when it is burned off during an annealing process.

2. The roll oil composition of claim 1 which contains about 0.05-2.0 percent by weight of a 2,4,6-trialkylated phenol.

3. In the cold rolling of metal which is subsequently to be annealed, the improvement which comprises preventing staining of the said metal during the rolling and subsequent annealing operations by supplying to the surface of the metal being worked a lubricant consisting essentially of a mineral lubricating oil of about 50-110 seconds Saybolt Universal viscosity at 100° F. which would normally permit staining of the metal to occur and about 0.5-3.0 percent by weight of tricresyl phosphate and about 0.001-0.5 percent by weight of an aliphatic dicarboxylic acid wherein the carboxy groups are separated by 1-4 carbon atoms and having a C₆₋₂₀ aliphatic hydrocarbon substituent group.

4. The process of claim 3 wherein the said lubricant contains about 0.5-2.0 percent by weight of a 2,4,6-trialkylated phenol.

5. A roll oil for use in the cold rolling of metals consisting essentially of a mineral lubricating oil of about 50-110 seconds Saybolt Universal viscosity at 100° F. containing about 1.5 percent by weight of tricresyl phosphate, about 0.015 percent by weight of alkenyl succinic acid having a branched chain C₁₂ hydrocarbon substituent group, and about 0.1-1.0 percent by weight of 2,6-ditertiary butyl-4-methylphenol.

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