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LUBRICANT USEFUL IN METAL WORKING

Michael C. Churn, Westcliff, England, assignor to Mobil Oil Corporation

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ABSTRACT OF THE DISCLOSURE

The stability of emulsified lubricant compositions is improved when there is present therein an aromatic oil and a mixture of mono- and dialkyl phosphates, the alkyl having from about 8 to about 20 carbon atoms. The emulsion lubricants containing such materials are useful in the cold rolling of steel.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is similar in subject matter to an application filed of even date herewith in the name of Robert H. Davis, entitled "Improved Lubricant for Metal Working," application Ser. No. 127,764, filed Mar. 24, 1971. The mentioned related application concerns an improvement in the hard water stability of metal working lubricants, the lubricants having therein a mixture of mono- and dioleyl phosphates and a lubricant consisting essentially of a lubricating oil, especially a mineral lubricating oil.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to emulsifiable lubricants useful in the rolling of metals. More particularly, the invention is concerned with providing such lubricants having improved stability properties, particularly in the emulsified form.

DESCRIPTION OF THE PRIOR ART

The most modern rolling procedures presently used to produce extremely thin gauge metal or strip products have increased the burden on the roll lubricants. The overriding necessity of obtaining increasingly higher gauge reduction per roll pass and at even faster rates than used in the past has increased the standard load-carrying and cooling requirements of roll oils even more so. Present commercial lubricants cannot perform adequately in the cold-rolling of steel, for example, wherein gauge reduction of over 80% are sought in a single mill throughput at a strip rate of above 1500 feet per minute. The rolling pressures are considerably greater therefore requiring lubricants to form tougher load-carrying films than hitherto known. The high degree of heat generating from the fast rolling rates must be dissipated quickly and thus the lubricant must be an equally effective coolant. The roll oil must also be able to remove metal fines from the metal being rolled to prevent marring the finished surface. Also the metal fines should be easily removed from the oil. If permitted to remain in the oil, they can cause metal surface defects in later rolling operations. The inability of an emulsion to collect fines adequately and the difficulty of removing those that are collected may be due to emulsion separation during metal working operations. Moreover, many known oils tend to remain on the metal surface during annealing, leaving severe stains thereon.

U.S. Pat. No. 3,071,544 describes rolling oil emulsions containing a number of components, including a small amount of an organic acid. The acid is either liquid or oil soluble or is reacted with other components in the formulation to provide oil soluble soaps, such as the soaps of alkanolamines. U.S. Pat. No. 3,311,557 describes

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emulsions for the hot rolling of nonferrous metals which contain a fatty acid, a polyol and ethanolamine. The ethanolamine reacts with the acid in sufficient proportion to provide a ratio of base number to acid number of from 0.15 to 0.4. Specific examples of this patent show the use of oil-soluble, liquid fatty acids.

U.S. Pat. 3,523,895 discloses metal working lubricants comprising a lubricating oil and an aryl or alkyl phosphate. U.S. 3,432,434 teaches a metal rolling lubricant containing an alkyl-aromatic hydrocarbon which might contain an alkali or alkaline earth metal phosphate or an amine phosphate.

SUMMARY OF THE INVENTION

In accordance with the invention, it has now been discovered that the stability of emulsion-type lubricants, especially in emulsion form, can be made more stable by employing a composition containing at least about 20% by weight, on a water free basis, of an aromatic oil and a lesser amount of a mixture of mono- and dialkyl phosphates, the alkyl having from about 8 to about 20 carbon atoms. Preferably, this will be a mixture of mono- and dioleyl phosphates. In addition, the lubricant contains a solid aliphatic monocarboxylic acid of from about 10 to about 30 carbon atoms.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The lubricant emulsions used in the cold rolling of metal in accordance with this invention broadly comprises from about 0.75% to about 10% by weight of an oil plus solid acid composition in water. The mixed oil-acid neat composition contains from about 20% to about 50%, preferably from about 20% to 40%, by weight of the solid acid. The oil-soluble phase, being about 80% to about 50% by weight of the oil-acid composition, includes an aromatic oil as hereinafter described, emulsifiers and emulsion stabilizers. The oil may constitute from about 20% to about 60%, preferably about 30% to about 80%, by weight of the neat composition. In addition, such aromatic oil may be mixed with other oils, such as naphthenic and paraffinic mineral oils, in which case they constitute a maximum of about one-half the amount of aromatic employed.

When the oil-acid composition is mixed with water, the oil-soluble components become emulsified in the water and the solid acid remains as solid particles adhered to the emulsified oil droplets. Hence the typical final lubricant emulsion of this invention consists of water, emulsified oil droplets, and the solid acid closely attached to the droplets.

With regard to the oil-soluble phase, the components include from about 1% to about 15% by weight of the oil phase of an alkanolamine having from about 2 to about 5 carbon atoms per alkanol group and from about 1% to about 15% by weight of the oil phase of an emulsifier preferably having a hydrophilic-lipophilic balance of at least 10. In addition to these two components, the oil phase may also contain from about 0.05% to about 2% by weight of an aromatic sulfonate and from about 2% to about 15% by weight of a mixture of mono- and dialkyl phosphates.

In the most preferred form, the oil-acid composition contains the components in the following percentages: (1) from about 30% to about 50% by weight of oil, either aromatic oil alone or a mixture thereof with another oil; (2) from about 20% to about 40% by weight of the solid aliphatic saturated monocarboxylic acid having from about 14 to about 28 carbon atoms; (3) from about 3% to about 12% by weight of an alkanolamine having from 2 to about 4 carbon atoms; (4) from about 5% to about

10% by weight of a mixture of mono- and dialkyl phosphates; (5) about 3% to about 12% by weight of an emulsifier having a hydrophilic-lipophilic balance of at least 10; and (6) from about 0.1% to about 1.5% by weight of an aromatic sulfonate.

It has been found that by using the components of the lubricant composition as a 0.75% to 10% emulsion there is provided a surprisingly effective lubricant-coolant which overcomes the arduous requirements encountered in the high speed cold-rolling of metals, such as steel. Mill speeds of between 4000 and 5000 feet per minute have been reached with the hereindisclosed lubricants. Furthermore, final gauge sizes of as low as 0.0075 inch have been attained at high mill speeds with the use of the lubricants of this invention.

One of the reasons for the effectiveness of these lubricants is believed to be the uniform distribution of such a large quantity of the solid monocarboxylic acid in the emulsion. Thus one aspect of this invention is directed to roll oil lubricants consisting of about a 0.75% to 10% by weight oil-in-water emulsion, wherein, as previously described, the neat phase, on a water-free basis, contains from about 20% to about 50% of said solid acid.

The mixing equipment needed for combining the components of this invention are of a conventional nature, known in the art. Preferably the oil, the water, the acid and the other components, with the exception of component (6), are mixed together initially at a temperature of from 50° C. to about 100° C., and preferably 80° to 90° C., for a sufficient period to obtain a uniform composition. From about 30 minutes to about 7 hours, preferably 1 hour, of mechanical mixing is ordinarily sufficient to obtain the desired emulsion mixtnre. It may be found necessary to subject the mixture to a particle size reduction step in order to obtain uniformity. Such a step may be carried out by means of suitable equipment for this purpose, such as a colloid mill, homogenizer and the like. The preferred mixing procedure is performed by first using a mechanical mixer and then the homogenizer, maintaining the temperature higher than 60, preferably from about 80° to about 90° C. The mixture is cooled rapidly to a temperature below 50° C., and the aromatic sulfonate is mixed in. The mixture may thereafter be submitted to a final homogenizing treatment.

Often mixing equipment is not readily available at the mill and, moreover, too much time may be spent at the mill in forming the emulsion lubricant. For the purpose of convenience and the saving of time and expense, a concentrated emulsion may be initially prepared by the supplier prior to shipment to the mill. For the best emulsion concentrate, that is, the compositions which will require the least mixing time in the mill equipment, compositions containing from about 20% to about 60% by weight of the above components (1) to (6) and from about 80% to about 40% by weight of water are preferred. These concentrates are simply diluted in further amounts of water to produce the 0.75% to 10% emulsion for use.

The components of the water free, or "neat" composition are discussed hereinafter. The finished formulations provide the unexpected results hitherto unavailable with conventional lubricants.

The aromatic oils useful in practicing this invention include all of the general group of oils which are furfural extracts having a viscosity within the range of about 10–150, preferably 30–70, SUS at 100° F. and a specific gravity greater than one. The aromatic content should be greater than 90% and its boiling point should be less than 650° F. to eliminate carcinogenic hazards.

Oils that may be used with the aforedescribed aromatic oils in the practice of this invention include both naphthenic and paraffinic mineral oils having a Saybolt viscosity in the range of 100 through 300 SUS at 100° F. and synthetic lubricants, such as synthetic ester lubricants, polyolefin fluids, alkylene oxide-derived fluids and the like.

From about 20% to about 50% by weight of neat composition is an aliphatic, saturated monocarboxylic acid having from about 10 to about 30, and preferably from about 14 to 28, carbon atoms. This range includes myristic, palmitic, stearic, arachidic, and behenic acids which are all normally solid, and insoluble in mineral oils and water. Preferably, stearic acid is employed. At elevated mixing temperatures and at mill operating temperatures these acids may become liquefied. However, at reservoir temperatures, it is believed that although the emulsions are stable, a heterogeneous system may result. It is therefore within the scope of this invention to use acids which may be in a solid and undissolved state, such as a large particle or suspensoid, at any point during the use or storage of the emulsion lubricant.

The alkanolamine is used as an emulsifying agent in the lubricant, in amounts ranging from about 1% to 15% and preferably 3% to 12% by weight of neat composition. Primary, secondary, and teritary alkanolamines may be used. Triethanolamine, isopropanolamine, triisopropanolamine, and isobutanolamine are examples of suitable compounds for use in this invention.

The phosphate used in the practice of this invention is a mixture of mono- and dialkyl phosphates where the alkyl contains from about 8 to about 20 carbon atoms and having concentrations of each component within well defined limits. The preferred member is a mixture of mono- and dioleyl phosphate. The concentration of monoalkyl phosphate, exemplified by monooleyl phosphate $[C_{18}OP(O)(OH)_2]$, will range between about 30 and about 45% of the phosphate mixture, and the concentration of dialkyl phosphate, as for example dioleyl phosphate $[(C_{18}O)_2P(O)OH]$, will constitute the remainder, i.e., from about 70 to about 55% of the mixture. The phosphates may be prepared in known ways. For example, the mono- and dialkyl phosphates can be made separately by reacting an alcohol with $POCl_3$ in the desired ratio, followed by forming the acid. The individually made components can then be combined to form the mixture of the invention. In addition, the mixed mono- and dialkyl phosphates can be made in one step by reacting the appropriate alcohol with P_2O_5, usually in the ratio of 3 moles of alcohol to 1 mole of P_2O_5. The alcohols used, as already implied, will contain from about 8 to about 20 carbon atoms. In preparing the phosphates of the invention, all the alcohol employed may have all carbon chains of the same length, or the alcohol may contain molecules ranging from the minimum chain length of 8 carbon atoms to the maximum of 20 carbon atoms. For example, the preferred "oleyl" alcohol, even the prime commercial grade, is not pure C_{18}, but is about 60% of unsaturated C_{18} with lesser amounts of C_{12}, C_{14}, C_{16} and C_{20} alcohols.

The concentration of the emulsifiers or emulsion stabilizers, preferably having a hydrophilic-lipophilic balance of at least 10 or higher, may range from about 1% to about 15% and preferably from about 3% to about 12% by weight. Included in this category of emulsifiers are cationic, anionic and nonionic emulsifiers, such as amines having from 4 to 36 carbon atoms and the C_4—C_{36}-alkyl phenols, and fatty or resin alcohols, fatty acids, esters and partial esters of fatty acids and polyols and fatty acid amides, each having from 4, and preferably from 8, to 36 carbon atoms. A preferred group of emulsifiers are the alkoxylated derivatives of the above-listed organic compounds obtained by reacting them with an alkylene oxide having from about 2 to 4 carbon atoms, such as ethylene oxide (also termed "ETO"). A preferred group of emulsifiers is the N-acyl-substituted dialkanolamides, the acyl group having 8 to 30 carbon atoms, such as lauroyl diethanolamide. Other emulsifiers include gum Arabic, often used in the preparation of wax emulsions.

The aromatic sulfonate acts as a control agent of the particle size and viscosity of the emulsion. It is present in relatively minor proportion, ranging from 0.05% to 2.0%, and preferably 0.05% to about 1.0%, by weight of the emulsion concentrate. The aromatic suklfonates include oil soluble metal salts of petroleum sulfonic acids and synthetic alkaryl sulfonic acids, particularly those having a molecular weight of from about 300 to 800. The preferred alkyl substituents on the aromatic ring contain from about 8 to 24 carbon atoms. The aromatic sulfonate used in the lubricants of this invention is an oil-soluble beta-naphthalene sulfonic acid-aldehyde condensate, and particularly useful is the formaldehyde condensate. Preparations for producing such condensates are generally known in the art. They may also be used in the form of an alkali metal salt.

In connection with the use of the lubricants of this invention, emulsion compositions containing additionally a liquid fatty acid, having from about 12 to about 22 carbon atoms, preferably oleic acid or linoleic acid, in combination with an aliphatc fatty acd amide having from about 10 to about 18 carbon atoms preferably lauroyl diethanolamide, possess further improved anti-corrosion properties in the cold-rolling of steei. Oleic acid offers additional oiliness characteristics which aid in the film-forming properties of the lubricant, but it does not provide any anti-corrosion protection by itself. It is know that amides do provide some anti-corrosion properties alone. However, in the presence of oleic acid, the fatty acid amide acts in an improved manner evidencing unusual cooperation, as between co-agents. The combination of oleic acid and lauroyl diethanolamide protects the surface of the metal strip against rust in a very effective manner. The oleic acid is used in minor quantities ranging from 1% to about 5% by weight of concentrate. The amide is used in amounts ranging from about 4% to about 8% by weight of concentrate.

As indicated heretofore, the compositions of this invention are particularly useful in the cold-rolling of steel, as well as in other metal-working operations. The lubricants herein described permit the high speed gauge reduction of the metal in metal rolling operations. They also provide an unusual improvement in removing metal fines caused in the rolling. It is well known that in rolling of metal, when the metal sheet is fed into rollers, small particles of metal may break off. These particles usually remain in the lubricant. When normal lubricants are used, the smaller particles, or fines, do not always settle out when the lubricant is passed into the reservoir of holding tank at the conclusion of the rolling operation. Hence, when the lubricant is used again, these fines may be carried onto the metal surface in the succeeding rolling operation and cause surface blemishes. While it is true that used lubricant is skimmed in the holding tank, it has been found that skimming does not always remove all of the metal fines, and in the finished metal strip may be marred. The performance of the emulsion lubricants of this invention is unique in that the presence of the solid acid may act to reject the metal fines from the emulsion and float them to the surface where they are removed in the skimming step.

It is theorized that at the point of maximum pressure in the rolling operation, or "the rolling point," a small portion of solid acid separates from the emulsion and is formed into flakes. It is at this point that the metal fines are also formed. It is believed that these metal fines are then mechanically or chemically taken off in the solid acid. The used oil, passing from the rollers into the skimming tank, contains both the emulsified oil and the adhered solid acid particles, free oil, and the solid acid flakes having the metal fines entrapped thereon. In the skimming tank, the free acid flakes containing the metal fines float to the surface where thye are mechanically removed, e.g., skimmed off, leaving the resulting emulsified composition almost completely free of metal fines. The larger metal particles which could not be entrapped by the acid flakes present little problem, since they usually do not remain dispersed in the emulsion but settle to the bottom of the holding tank by gravity. Hence, in the suceeding rolling operations, there are essentially no metal particles, including the fines, present in the oil which can mar the surface of the rolled metal, thereby producing metal strips having almost mirror-like appearance.

The following examples show how the lubricants of this invention are prepared and utilized:

EXAMPLE 1

	Parts by weight	
	Emulsion	Neat
Mineral oil [1]	8.6	27.6
Mineral oil [2]	5.4	17.4
Acid [3]	9.0	28.9
Lauroyl diethanolamide	2.0	6.4
Triethanolamine	4.0	12.8
Tricresyl phosphate	2.0	6.4
Naphthalene sulfonate-formaldehyde condensate	.15	.5

[1] Naphthenic oil having a viscosity of 100 SUS at 100° F.
[2] Solvent refined paraffinic oil having a viscosity of 100 SUS at 100° F.
[3] Hydrogenated tallow fatty acids having the composition (weight percent); 1-3% C_{14}: 23-33% C_{16}: and 65-77% C_{18}

All the components, except for the sulfonate-formaldehyde condensate, were combined under agitation with sufficient water to provide the 30% emulsion. The mixing was performed for about 1 hour, at about 80° to 90° C. The mixture was then passed through a Manton-Gaulin homogenizer for an additional hour. The resulting emulsion was cooled and the condensate was added over a half-hour period, with agitation, at a temperature below 50° C. The cooled mixture was again passed through the homogenizer, while maintaining the temperature below 50° C., for 1 hour.

The storage stability of this emulsion at elevated temperatures was estimated by heating the emulsion to 150° F. and measuring the time it took for the emulsion to split. Under this temperature condition, only 1–2 hours were required for the emulsion to split.

EXAMPLE 2

This example shows the effect on storage stability using ingredients shown in Example 1, but with mixed oleyl phosphates. Preparation of composition and testing conditions were the same as set forth in Example 1.

	Parts by weight
Mineral oil [1]	8.60
Mineral oil [2]	5.40
Acid [3]	9.00
Lauroyl diethanolamide	1.00
Triethanolamine	4.00
Mixed oleyl phosphate [4]	2.00
Naphthylene sulfonate-formaldehyde condensate	.15
Water	69.85

[1] Naphthenic oil having a viscosity of 100 SUS at 100° F.
[2] Solvent refined paraffinic oil having a viscosity of 100 SUS at 100° F.
[3] Hydrogenated tallow fatty acids having the composition (wt. percent):
1–3% C_{14}; 23–33% C_{16}; and 65–77% C_{18}
[4] About 40% monooleyl and 60% dioleyl.

The following examples (3–6) illustrate the use of aromatic oil, either alone or in combination with the conventional naphthenic oil of Examples 1 and 2. The compositions were prepared and the testing was conducted substantially in accordance with Example 1.

	Parts by weight			
	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Mineral oil [1]			5.0	5.0
Aromatic oil [2]	14.0	5.0	5.0	5.0
Acid [3]	8.0	8.0	8.0	8.0
Lauroyl diethanolamide	1.0	1.0	------	1.0
Triethanolamine	4.0	4.0	4.0	4.0
Mixed oleyl phosphates	2.0	2.0	2.0	2.0
Naphthalene sulfonate-formaldehyde condensate	.15	.15	.15	.15
Water	70.85	79.85	75.85	74.85

[1] Napthenic oil having a viscosity of 100 SUS at 100° F.

[2] The aromatic oil used contained 95.2% of aromatics, 3.9% of polar resins. It had the following properties; Viscosity, SUS at 100° F., 50: Specific gravity, 1.046: Pour point, −40° F.: Mixed aniline point, 63° F.: Refractive index at 20° C., 1.605.

[3] Hydrogenated tallow fatty acids having the composition (weight percent); 1–3% C_{14}: 23–33% C_{16}: and 65–77% C_{18}.

In each case involving Examples 3–6, the emulsions were still stable after 3 months at 150° F.

Under actual production conditions, the Example 6 composition has given consistently improved quality of cold-rolled steel, both low carbon and alloy steels. The improved quality is manifested by much improved brightness and cleanliness after annealing.

I claim:

1. An improved emulsifiable lubricating composition made by mixing from about 20% to about 50% by weight of a solid aliphatic monocarboxylic acid having from about 10 to about 30 carbon atoms, from about 1% to about 15% by weight of an alkanol-amine having from 2 to 4 carbon atoms in the alkanol group, from about 0.05% to about 2 by weight of an aromatic sulfonate, from about 2% to about 15% by weight of a phosphate, the remainder being an oil, wherein said phosphate is a mixture of monoalkyl phosphate and dialkyl phosphate, the said alkyl containing from about 8 to about 20 carbon atoms, and the said oil is an aromattic oil alone or in admixture with other oils wherein said other oils are present up to a maximum of about 50% of said aromatic oil, the aromatic oil having an aromatic content greater than 90% and a viscosity within the range of about 10–150 SUS at 100° F.

2. The composition of claim 1 wherein said phosphate is a mixture of monooleyl phosphate and dioleyl phosphate.

3. The composition of claim 1 wherein the solid acid contains from about 14 to about 28 carbon atoms.

4. An emulsion lubricant concentrate composition comprising from about 20% to about 60% by weight of the composition of claim 1 and from about 80% to about 40% by weight of water, wherein the said solid acid remains as a solid component in the said emulsion composition.

5. An emulsion lubricant composition comprising from about 0.75% to about 10% by weight of a composition of claim 1 and from about 99.25% to about 90% by weight of water, wherein the said solid acid remains as a solid component in the said emulsion composition.

6. The composition of claim 1 wherein the said solid acid is stearic acid.

7. The composition of claim 1 wherein the said alkanolamine is triethanolamine.

8. The composition of claim 1 wherein the said emulsifier is lauroyl diethanolamide.

9. The composition of claim 1 wherein the aromatic sulfonate is a naphthalene sulfonate-formaldehyde condensate.

10. The composition of claim 9 wherein the said condensate is in the form of an alkali metal salt thereof.

11. The composition of claim 2 wherein said monooleyle phosphate is present in said mixture to the extent of between about 30% and about 45% by weight thereof.

12. The composition of claim 2 wherein said dioleyl phosphate is present in said mixture to the extent of between about 70% and about 55% by weight thereof.

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DANIEL E. WYMAN, Primary Examiner

W. H. CANNON, Assistant Examiner

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