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NONCORROSIVE SOLUBLE OIL CONTAINING ACTIVE SULFUR

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This invention relates to an emulsifiable lubricant comprising a mineral lubricating oil which disperses readily in the presence of water, and more particularly to a soluble oil for use as a cooling and lubricating fluid in metal working operations, such as the cutting, grinding and turning of metals.

With the use of higher machine speeds in cutting and grinding operations, and the desire to take larger or deeper cuts, the operations frequently become too severe to be handled satisfactorily by the conventional type of soluble oil composed of mineral lubricating oil with the customary emulsifying agent or soap. Since it was found in the case of non-emulsifiable cutting fluids that improved performance on severe machining operations could be achieved by imparting extreme pressure properties to the cutting fluid, naturally it was assumed that this would apply to emulsifiable cutting fluids also. In order to provide extreme pressure properties or added load-carrying capacity, it has heretofore been suggested that a sulfurized base, such as a sulfurized mineral lubricating oil, be employed in an emulsifiable lubricant or soluble oil of this character. In order to obtain the required extreme pressure properties, it has been found desirable to employ a sulfurized mineral lubricating oil containing loosely combined active sulfur as opposed to the use of sulfurized fatty oils or fats sulfurized under high heat and/or pressure providing tightly bound or combined sulfur. The production of mineral lubricating oils containing about 0.5 to 4.0% of loosely combined active sulfur is well known as illustrated by the Kaufman Patent No. 2,167,439, wherein the mineral lubricating oil is heated with the required proportion of free sulfur in the absence of a fatty oil and at atmospheric pressure at a controlled temperature of about 300–360° F. for a period of time of about 1–4 hours to fix the sulfur in the oil in a loosely bound active form. While this type of sulfurized mineral lubricating oil is preferred, it is to be understood that mineral lubricating oils sulfurized under high heat conditions, or sulfurized in the presence of a small proportion of fatty oil, can also be used for purposes of the present invention provided the mineral oil contains some loosely combined or active sulfur. Thus the mineral lubricating oils may or may not contain tightly bound sulfur in addition to a content of loosely combined or active sulfur of at least about 0.25% or higher. When a sulfurized mineral oil containing active sulfur of this type is employed as a proportion or all of the lubricating base of the soluble oil, which is diluted with water at the time of use to provide emulsions containing from about 5 to 50 or more parts of water to one of oil, the active sulfur in the presence of water results in objectionable

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corrosion of ferrous metals or steel employed in the work.

One of the principal objects of the present invention is to provide an emulsifiable lubricant containing active sulfur affording extreme pressure properties or increased load carrying capacity, and which at the same time is effectively inhibited against steel corrosion in the presence of water.

Another object of the present invention is to provide a soluble oil having as a major constituent sulfurized mineral lubricating oil with loosely combined active sulfur, and which is substantially non-corrosive with respect to steel in the presence of water.

Another object of the present invention is to provide an improved method of compounding a soluble oil of this character in order to produce a soluble oil with superior extreme pressure properties in an economical manner.

Other objects and advantages of the invention will be apparent from the following description and the appended claims.

In accordance with the present invention, a superior soluble oil possessing extreme pressure properties is provided by mixing a sulfurized mineral lubricating oil containing loosely combined active sulfur with an unsulfurized mineral lubricating oil solution of the soap or other emulsifying agent, said solution containing a small proportion of water as well as a high boiling organic liquid coupling agent or mutual solvent, the two being mixed in such proportions that the sulfurized mineral lubricating oil is the major constituent of the composition; and then inhibiting the soluble oil against steel corrosion in the presence of water by adding a small amount in excess of about 0.1% by weight of an organic amine containing an alkylene polyamine group having from 3 to 20 carbon atoms in the group.

The sulfurized mineral lubricating oil ingredient is separately formed from the soap-emulsifying base. The lubricating oil employed for sulfurization may vary considerably in basic type, viscosity or degree of refining, depending on the grade or viscosity of the ultimate soluble oil desired. This oil is preferably mixed with about 0.75–3.0% of free sulfur and the mixture heated at about 300–340° F. for a period of about 1–4 hours to obtain a sulfurized mineral lubricating oil containing about 0.75–3.0% by weight of loosely combined active sulfur.

The emulsifier employed in the composition may comprise any of the conventional alkali metal or amine soaps or mixtures thereof customarily employed in soluble oils and capable of promoting the formation of an oil-in-water emulsion, such as natural or synthetic carboxylates, sulfonates, resinates and naphthenates. In addition, the various synthetic or non-soap emul-

sifiers which are well known in the detergent field, including the hexahydric alcohol partial esters of high molecular weight fatty acids and the anhydrides thereof, such as sorbitan mono-oleate, can also be employed for this purpose, either alone or in combination with a soap emulsifier. Preferably, a soap emulsifier is used which comprises a sodium mahogany sulfonate, which is a sodium soap of the oil-soluble sulfonic acids obtained in the sulfuric acid treating of petroleum hydrocarbons. A very satisfactory soap-emulsifier in accordance with the present invention comprises a mixture containing substantial proportions each of sodium mahogany sulfonate, sodium resinate and sodium naphthenate. A proportion of about 10–20% by weight of soap, or mixture of soaps, is ordinarily employed on the basis of the soluble oil composition and preferably about 15% by weight.

The preferred soap base specified above is conveniently prepared by forming a solution in unsulfurized mineral lubricating oil, preferably a light oil having a Saybolt Universal viscosity at 100° F. of about 70–150 seconds of rosin, naphthenic acids and sodium sulfonate, and then saponifying this solution by heating with an aqueous caustic solution. It is pointed out that the mahogany sulfonic acids are conveniently recovered in purified form as a solution of sodium mahogany sulfonate in non-saponifiable mineral lubricating oil.

As noted above, the sulfurized mineral lubricating oil is purposely not utilized as make-up oil to form the solution of the rosin, naphthenic acids and sodium sulfonate. It has been found that, when the rosin and/or naphthenic acids were saponified with the aqueous alkali or caustic soda solution in the presence of the sulfurized mineral lubricating oil, there was an excessive consumption of the alkali, and at the same time a product was obtained which was difficultly emulsifiable and had poor emulsion stability. Apparently the caustic soda reacts with the active sulfur of the sulfurized mineral lubricating oil, and the formation of reaction products gives rise to the emulsification difficulties. Consequently, a sulfurized mineral lubricating oil is separately formed, and the soap base is completely saponified in the absence of the sulfurized lubricating oil. It is preferable to utilize about the minimum amount of unsulfurized mineral lubricating oil as will insure proper liquefaction of these constituents for the subsequent saponification; and for this purpose the amount of unsulfurized mineral lubricating oil is preferably adjusted to obtain an ultimate total soap content following saponification which is around 50% by weight. Ease of handling is the only limitation to the soap content of the base, and a more concentrated or less concentrated soap base can be used, if desired. The required proportion of the soap base is ultimately added to the sulfurized mineral lubricating oil to give the desired soap content in the finished soluble oil, and at the same time the sulfurized mineral lubricating oil will constitute the major constituent of the soluble oil, generally about 60–70% thereof by weight, to provide high extreme pressure properties. It will be understood that where liquid emulsifiers are used, the addition of unsulfurized mineral lubricating oil to form the emulsifier base solution is not required; and the proportion of surfurized mineral lubricating oil in the soluble oil composition can thereby be further increased, such as up to about 80% or somewhat higher. Also the preformed soaps can be compounded with the sulfurized mineral lubricating oil, thereby enabling the proportion of the latter in the ultimate soluble oil composition to be increased.

It is found desirable to have the ultimate soluble oil slightly on the acid side, and for this purpose, an excess of naphthenic acids is used to provide a neutralization number of about 1–3 in the soap base. Effective control is ordinarily and conveniently secured by adding additional free naphthenic acids over and above the amount required for production of the desired amount of naphthenate soap either prior to or following completion of the saponification reaction. Ordinarily, an amount up to about 0.8% by weight of free naphthenic acids will be present in the finished soluble oil.

As is well known, soluble oils are usually prepared in the form of a concentrated emulsion or colloidal solution containing a minium quantity of water to enable the oil, at the time of use, to rapidly take up additional quantities of water to form the dilute 5:1 to 100:1 emulsions customarily employed for the cooling and lubrication of the metal working operations. In order to form a concentrated soluble oil of this character which is stable in storage against separation of ingredients, a small proportion of the order of 0.4–1.0% of a high boiling organic liquid coupling agent or mutual solvent is added to the soluble oil. Examples of very satisfactory coupling agents of this character are the monobutyl ethers of ethylene glycol and diethylene glycol, various alkylene glycols, and esters and ethers thereof. This coupling agent may be added to the soap base following saponification, or it can be added following the addition of the sulfurized mineral lubricating oil.

In addition, the water content of the concentrated soluble oil is also found rather critical for storage stability, and varies between about 1–4% by weight of the soluble oil depending on the soap or emulsifier content and the amount of coupling agent employed. In order to effect saponification of the rosin and naphthenic acids and conveniently maintain the water content within the stable range, a rather concentrated caustic soda solution, such as one of 49% strength, is employed. Following saponification, additional water may be added along with the organic liquid coupling agent to the soap base, or to the mixture of soap base with sulfurized mineral lubricating oil, to adjust the water content within the most stable portion of the effective range.

In accordance with the present invention, the soluble oil is rendered non-corrosive with respect to ferrous metals such as steel by incorporating therein about 0.1–2.0% of an alkylene polyamine having from 3 to 20 carbon atoms in the molecule, or an organic amine having such an alkylene polyamine group. By "alkylene" it will be understood that this refers to the source of the hydrocarbon group as being formed from an olefin, and not to any unsaturation of the hydrocarbon group as it exists in the compound, since the unsaturation of the original olefin or alkylene group is consumed in the formation of the polyamino compound. This follows the usual nomenclature as exemplified by propylene diamine, where the original unsaturation of the propylene is taken up or satisfied by the addition of two amino groups to the propylene nucleus. Included within this group of alkylene polyamines which are employed as corrosion inhibitors in accord-

ance with the present invention are the polymethylene diamines from trimethylene diamine up to decamethylene diamine, including the diamines of tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, and nonamethylene. In addition, one or more hydrogen atoms of the polymethylene nucleus of the foregoing compounds can be substituted by amino groups, as exemplified by hexamethylene tetramine wherein two of the hydrogen atoms of the hexamethylene nucleus in hexamethylene diamine are substituted by amino groups.

In addition to the foregoing straight chain polymethylene polyamino compounds set forth above, the branch chain olefin polyamino compounds having from 3 to 20 carbon atoms in the molecule are also suitable for purposes of the present invention. Examples of this type include propylene diamine, butylene diamine, pentylene diamine, hexaylene diamine, octylene diamine such as diisobutylene diamine, triisobutylene diamine and tetraisobutylene diamine. Moreover, one or more of the hydrogen atoms of the branch carbon chain of the foregoing compounds can be substituted by amino groups such as propylene triamine, butylene tetramine and the like.

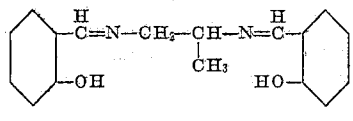
Another very satisfactory sub-group of compounds falling within this class of effective compounds for purposes of the present invention are those termed herein aliphatic polyolefin polyamines having 4 to 20 carbon atoms in the molecule and which include an NH group or groups within the carbon chain in addition to the terminal NH_2 groups. These are formed by a condensation reaction, as exemplified by the condensation of two molecules of ethylene diamine producing diethylene triamine,

$$H_2N\cdot C\cdot C\cdot \underset{H}{N}\cdot C\cdot C\cdot NH_2$$

with the splitting off of NH_3. Further condensation produces triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, etc. which are also highly effective for purposes of this invention. Similar condensation products of propylene diamine, butylene diamine, etc. can likewise be employed.

Moreover, any of the foregoing compounds can be further substituted by replacing a hydrogen atom attached to a carbon with an alkyl, a hydroxy alkyl or an amino alkyl group, such as dibutyl diethylene triamine, hydroxy ethyl ethylene diamine, amino methyl propylene diamine, etc. All of the foregoing compounds are termed for convenience in the following description and claims "aliphatic alkylene polyamines." From the standpoints of effectiveness and availability the aliphatic polyethylene polyamines are preferred; and, of these, diethylene triamine is selected from the standpoint of cost.

The foregoing are all aliphatic saturated alkylene polyamines. In addition, effective inhibitors for purposes of the present invention are formed by substituting an aryl or cyclic group or groups for one or both of the hydrogen atoms of the terminal amino groups of an alkylene polyamine. For example, a methyl benzene or methyl phenol group or groups may replace one or both of the hydrogen atoms of the terminal amino groups of an alkylene diamine. This is illustrated by disalicylal propylene diamine having the formula



It will be noted that this compound contains a salicylal group substituted for the two hydrogen atoms through a double bond on each of the nitrogen atoms of the terminal amino groups of propylene diamine and is a condensation product of propylene diamine with salicylaldehyde. It has been found that a somewhat higher proportion of at least about 0.2% by weight and preferably about 0.4% by weight based on the soluble oil of this sub-group of inhibitors is required for the desired corrosion inhibition of steel in the presence of water, although proportions up to 2% can be employed. Other examples of inhibitors of this type are dibenzyl ethylene diamine, disalicylal butylene diamine, and disalicylal trimethylene diamine.

In addition, a bacteriostatic agent as well as an odorant, both of conventional character, may be added to the finished soluble oil in proportions of about 0.4–0.8% and 0.01–0.1% by weight respectively. Any suitable bacteriostatic agent known to control or inhibit bacterial growth in soluble oil emulsions, such as 2,3,4,6-tetrachlorophenol, and any suitable essential oil or other odorant which imparts a pleasing odor to the composition may be employed.

The composition of the preferred type of soluble oil prepared in accordance with the present invention may fall within the following percentage limits by weight based on the soluble oil, with the preferred range being also indicated:

Ingredients	Percentage limits	Preferred range
Sulfurized mineral lubricating oil with loosely combined active sulfur.	50–85	60–70
Unsulfurized mineral lubricating oil	35–0	20–10
Sodium mahogany sulfonate	3–15	4–6
Sodium resinate	6–0	4.5–5.5
Sodium naphthenate	6–0	4.5–5.5
Free naphthenic acids	0–0.8	0.2–0.5
High boiling organic liquid coupling agent	0.4–1.0	0.5–0.8
Alkylene polyamine or organic amine containing alkylene polyamine group.	0.1–2.0	0.1–1.0
Water	1–4	2–3
Bacteriostatic agent (optional)		0.4–0.8
Odorant (optional)		0.01–0.1

By way of specific example, the preparation of a comparatively heavy or viscous soluble oil which has proved very satisfactory in service, was carried out as follows: A viscous naphthene base mineral lubricating oil was selected for sulfurization. This was carried out by mixing the oil with 1% free sulfur by weight while the oil was maintained at a temperature of 300–310° F. with stirring, followed by 1½ hours of soaking at this temperature with continued stirring. Under these conditions, the sulfur so added was almost entirely dissolved or loosely combined in an active form in the oil, so that it would show up in a standard test for free sulfur as distinguished from combined sulfur. Tests obtained on the original mineral lubricating oil and the resulting sulfurized oil are as follows:

Tests	Lubricating oil	Sulfurized oil
Gravity, ° API	18.6	17.9
Flash, Cleveland open cup, ° F	405	390
Fire, Cleveland open cup, ° F	455	447
Viscosity, Saybolt Universal at 100° F., sec.	790	786
Viscosity, Saybolt Universal at 210° F., sec.	58.8	58.5
Pour, ° F	−10	−10
Total sulfur, percent	0.20	1.38
Free sulfur, percent		1.2

The soap base for this soluble oil batch was prepared as follows: 674 pounds of a lubricating oil solution of sodium mahogany sulfonate an-

alyzing 32.8% by weight of sodium sulfonate, the balance being non-saponifiable mineral lubricating oil, were charged to a compounding kettle. Gum rosin having a saponification number of 170 was then charged to the kettle in the amount of 196 pounds; following which 337 pounds of naphthenic acids were added, the latter having a saponification value of 99 and non-saponifiable content of 31.4% by weight consisting essentially of mineral lubricating oil. In addition, 65 pounds of a light naphthene base mineral lubricating oil were added, as based on calculations to bring the ultimate soap content following saponification to around 50% by weight. The added mineral lubricating oil had the following tests:

Gravity ° A. P. I.	23.1
Flash Cleveland open cup ° F.	315
Viscosity Saybolt Universal at 100° F., sec.	74.9
Pour ° F.	Pouring at —50

The steam was turned on to the kettle and the stirrers started, with heating being continued for about ½ hour until the kettle contents had been raised to a temperature of 245–260° F. and the added rosin had dissolved. The steam was then turned off and cooling water turned on to the kettle jacket to cool the contents to about 175° F.; when a 49% caustic soda solution was charged to the kettle in the amount of 92 pounds for saponification. This required approximately an hour at a temperature of 175–150° F.

Samples of the resulting lubricating oil solution of mixed sulfonate, resinate and naphthenate soap were withdrawn for tests to determine the required amount of naphthenic acids to be added to adjust the neutralization number of the batch to around 2.0, as well as to determine the required amount of additional water needed to adjust the water content of the completed soluble oil to about 2.3%. For this purpose, 13.7 pounds of the above-described naphthenic acids and a total of 82.5 pounds of additional water were required. In the procedure followed in this particular batch, the naphthenic acids were first added to adjust the neutralization number. Then 2836 pounds of the above described sulfurized mineral lubricating oil were stirred into the mix while maintained at a temperature of about 220–150° F., and 36 pounds of water were added as the batch cooled. In order to complete the preparation, 25.5 pounds of ethylene glycol monobutyl ether were added when the batch had cooled to about 110° F.; and finally at substantially room temperature 46.5 pounds of water together with 8.5 pounds of diethylene triamine were stirred in, the final addition of water being required to adjust the water content to the desired figure and compensate for some evaporation which had taken place.

The resulting soluble oil had a green color with a musky ammoniacal amine odor. The composition of the finished soluble oil in percent by weight was:

Sulfurized lubricating oil	66.5
Unsulfurized lubricating oil including non-saponifiable oil from the added sodium sulfonate and naphthenic acids	14.9
Sodium sulfonate	5.2
Sodium resinate	4.9
Sodium naphthenate	4.9
Free naphthenic acids	0.5
Ethylene glycol monobutyl ether	0.6
Diethylene triamine	0.2
Water	2.3

Tests obtained on this particular batch of soluble oil were as follows:

Color, Lovibond ½" cell	840.
Viscosity Saybolt Universal at 100° F., sec.	2,787.
Stability of water emulsions	Completely stable in all proportions.
Color of emulsion	Greenish white.
Low temperature stability	No separation.

Test on SAE load tester at 500 R. P. M.

Water-oil ratio emulsions strength:

	Pounds
Oil only	5,500
2–1	2,030
5–1	1,760
10–1	1,700
20–1	1,710
50–1	1,700

Corrosion test

Low carbon steel oil only	Slight green film OK.
5–1 emulsion	OK.
10–1 emulsion	OK.

The SAE test of the foregoing table was carried out with the standard SAE load tester utilized for determining the extreme pressure properties of lubricants, except modified as follows: A small storage tank containing the soluble oil or soluble oil emulsion under test was mounted about 3 feet above the Timken cups of the SAE machine. A ⅛" pipe connected to the tank served to deliver the emulsion to the test cups through a suitable valve. The discharge end of the pipe was fitted with a piece of ⅛" copper tubing flattened at the discharge end to form a slit opening, which served as a nozzle to deliver a flat stream of the emulsion to the cups. The end of the nozzle was arranged approximately one inch from the line of contact of the Timken cups and the stream of emulsion was directed so that it would strike the top cup just above the line of contact. In this manner, a stream of the fresh test lubricant was fed to the test cups during the entire period of the run, and simulated the normal procedure for applying soluble oil emulsion in the case of metal machining or grinding. The foregoing test shows the soluble oil to possess extreme pressure properties even in dilute emulsion form. It will be appreciated, in accordance with the standard SAE test, that the higher the rating number, the better is the extreme pressure property of the lubricant; and that the soluble oil alone rated above the test limit of the SAE machine.

The corrosion test of the foregoing table is a measure of the corrosiveness of the soluble oil or soluble oil emulsion to ferrous metals, such as steel. In the case of the soluble oil alone, the test was carried out by placing a metal strip, approximately 3 inches long and ¼ inch wide in a tall form 4 oz. bottle, with about ⅔rds of the strip covered with the oil to be tested. The bottle was then tightly stoppered and allowed to stand vertically at a temperature of 120±5° F. for a period of 168 hours, following which the metal strip was removed from the bottle and washed with water. The specimen was then examined visually for evidence of discoloration, etching and pitting. Only a slight discoloration is allowable and no pitting or etching should be present. The test on the emulsion of the soluble oil was carried out in the same manner, except that the metal strip was completely covered with the emulsion under test. The foregoing tests show that the soluble oil and the water emulsions prepared

therefrom were non-corrosive with respect to the low carbon steel specimen.

the tests shown in the table were of different duration and at other temperatures as indicated.

TABLE I

Inhibitor	Conc. in oil	Emulsion strength	Days in oven at— 100° F.	120° F.	160° F.	Appearance of steel strip
None	------	5-1	----	2	----	Heavy black flaked corrosion.
Diethylene triamine	0.2	5-1	----	7	----	Possibly a few dark specks—OK.
Triethylene tetramine	.2	5-1	----	6	----	OK.
Hydroxy ethyl ethylene diamine	.2	5-1	----	4	----	OK.
Hexamethylene tetramine	.2	5-1	----	7	----	OK.
Propylene diamine	.2	5-1	----	6	----	OK but a few spots.
Disalicylal propylene diamine	.4	5-1	----	7	----	OK.
Tetramethyl diamino diphenyl methane	.5	5-1	----	2	----	Black—corroded.
Sodium nitrite	.2	5-1	----	3	----	Badly blackened and corroded.
Zn dibutyl dithiocarbamate	.2	5-1	----	3	----	Black—corroded.
Urea	.2	5-1	----	2	----	Black.
Thiourea	.2	5-1	----	3	----	Do.
Diphenyl guanidine	.2	5-1	----	3	----	Do.
Cyclohexyl phosphite	.2	5-1	----	2	----	Black and corroded.
Triethanolamine	.2	10-1	25	----	1	Heavy Black corrosion.
Acetamide	.2	5-1	----	3	----	Black.

Other tests carried out on the said soluble oil showed it to have satisfactory hard water stability and ease of emulsification, and to be satisfactory in anti-rust properties.

While the foregoing soluble oil containing a small amount of diethylene triamine was satisfactorily non-corrosive, this soluble oil in the absence of such an effective inhibitor is objectionably corrosive to ferrous metals such as steel. Moreover, it was found by extended tests that corrosion inhibitors previously employed in conjunction with sulfur containing additives in lubricating oils proved entirely ineffective in this new environment of a soluble oil involving the presence of substantial amounts of water. In these tests, the organic amines containing an alkylene polyamine group having at least 3 carbon atoms in the group as defined above were found universally effective as non-corrosives in this new environment. This is illustrated in the following table which sets forth the results of the above described corrosion test on samples of the said soluble oil of the specific example, except that either no inhibitor was employed or else a different inhibitor was substituted in the indicated percent by weight for the diethylene triamine of the specific example. While the standard corrosion test described above employed a time of 7 days at a temperature of 120° F., certain of

The foregoing table sets forth by way of example members of the different sub-groups of effective organic amines containing an alkylene polyamine group of the present invention. In addition, the table illustrates the unsatisfactory results obtained with certain representative types of corrosion inhibitors as previously employed in mineral lubricating oil in other relationships. While an aliphatic alkylene polyamine, such as ethylene diamine, has heretofore been suggested as a color inhibitor for a lubricating oil of the type of a motor oil or turbine oil when used in proportions substantially less than 0.1% by weight, it was not to be anticipated that these higher molecular weight alkylene polyamines would function in a substantially higher proportion range for the new purpose of inhibiting corrosion of steel in the presence of water in the new environment of an emulsifiable lubricant containing active sulfur. The results are all the more unexpected since corrosion inhibitors previously employed in other relationships proved entirely ineffective in this new environment.

As illustrative of the effect of varying the proportion range of the corrosion inhibitor, results obtained on the preferred diethylene triamine and also on disalicylal propylene diamine in the soluble oil of the above example and on the uninhibited soluble oil are set forth in the following Table II:

TABLE II

Inhibitor	Conc. in oil	Emulsion strength	Days in oven at— 120° F.	160° F.	Appearance of steel strip
None	------	5-1	----	2/3	Failed.
Do	------	5-1	7	----	Do.
Diethylene triamine	0.2	5-1	7	----	Possibly a few dark specks on strip.
Do	.01	5-1	3	----	Completely covered by a thin black Coat.
Do	.05	5-1	4	----	Black.
Do	.2	5-1	7	----	OK.
Do	.2	5-1	7	2	Very thin black coat.
Do	.5	5-1	7	----	OK.
Do	.5	5-1	7	2	Very thin black coat.
Do	1.0	5-1	7	----	OK.
Do	1.0	5-1	7	2	Slightly discolored.
Do	.2	2-1	1	2	Bright—OK.
Do	.2	10-1	1	2	Do.
Do	.2	20-1	1	2	Covered with a soft thin black coat.
Do	.2	50-1	1	2	Do.
Do	.2	5-1	----	2/3	OK.
Disalicylal propylene diamine	.2	5-1	7	----	Failed.
Do	.4	5-1	7	----	OK.
Do	.2	5-1	----	2/3	OK.
Do	.4	5-1	----	2/3	OK.

The corrosion tests of the foregoing table were made in the same manner as described above for the soluble oil emulsion. In addition, some of the samples which had been exposed for the indicated period of time at 120° F. were then subjected to a further exposure at 160° F. for the period shown, in order to provide a more rigorous test. The results of the table show that a proportion of at least about 0.1% by weight of the diethylene triamine and at least about 0.2% by weight of the disalicylal propylene diamine is essential to afford proper protection against steel corrosion. For the customary service with the more concentrated emulsions, a proportion of around 0.2% and 0.4% by weight respectively appears sufficient, although higher proportions up to about 1–2% may be employed where more rigorous conditions are encountered.

By way of further example, the following is listed as representative of a soluble oil prepared in accordance with the present invention and which has proved very satisfactory in service:

	Percent by weight
Sulfurized mineral lubricating oil containing about 1% by weight of loosely combined active sulfur	66.6
Unsulfurized mineral lubricating oil	14.075
Sodium mahogany sulfonate	5.2
Sodium resinate	4.9
Sodium naphthenate	4.9
Free naphthenic acids	.5
Ethylene glycol monobtuyl ether	.6
Diethylene triamine	.2
Water	2.4
2,3,4,6-tetrachlorophenol	.6
Blend of essential oils known as "Fritzsche Compound No. 08219" manufactured by Fritzsche Bros. Co	.025

The addition of the essential oil blend as an odorant, and of the 2,3,4,6-tetrachlorophenol as a bactericide improve the product by masking the ammoniacal musky odor of the inhibitor, and serving to prevent the formation of emulsion odors by bacterial action. In the formula set forth above utilizing the 2.4% water content, it was found advisable to incorporate the 2,3,4,6-tetrachlorophenol in the soap base and adjust the neutralization number to about 2.0 prior to the addition of the sulfurized lubricating oil. However, the bactericide can be added to the finished soluble oil, in which case it is desirable to increase the water content by approximately 1% from that shown for added stability. The first method is preferred since, as a general proposition, soluble oils of higher water content are less satisfactory from a storage stability standpoint than those of lower water content.

Another very satisfactory soluble oil which has been extensively tested with good results was made by substituting 0.4% by weight of disalicylal propylene diamine for the 0.2% diethylene triamine in the formulation listed immediately above, reducing the unsulfurized mineral lubricating oil content accordingly. This particular soluble oil was clear dark red in color and of satisfactory odor, storage stability and freedom from sedimentation. While the present invention has been particularly described above as applied to a so-called soluble oil, it is to be understood that the invention is more generally applicable to an emulsifiable lubricant containing loosely combined or active sulfur, together with an oil-in-water emulsifier, and wherein it is desired or required that the lubricant be non-corrosive to ferrous metal in the presence of water.

The above described emulsifiable lubricant or soluble oil containing the species of aliphatic alkylene polyamine corrosion inhibitor is claimed in divisional application Serial No. 274,494, filed March 1, 1952.

Obviously many modifications and variations of the invention as above 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 soluble oil comprising as the major constituent sulfurized mineral lubricating oil containing loosely combined active sulfur, an emulsifying agent capable of promoting the formation of an oil-in-water emulsion, water, a high boiling organic liquid coupling agent, and about 0.2–2.0% by weight based on the soluble oil of an aromatic alkylene diamine selected from the group consisting of benzyl alkylene diamines and salicylal alkylene diamines effective to inhibit said soluble oil against steel corrosion in the presence of water.

2. A soluble oil according to claim 1, wherein the said aromatic alkylene polyamine is disalicylal propylene diamine.

3. A soluble oil according to claim 1, wherein the sulfurized mineral lubricating oil contains about 0.75 to 3.0 per cent by weight of loosely combined active sulfur and is present in a proportion of about 50–85 per cent by weight based on the soluble oil.

4. A soluble oil consisting substantially essentially of the following constituents in per cent by weight based on the soluble oil:

Sulfurized mineral lubricating oil with loosely combined active sulfur	50–85
Unsulfurized mineral lubricating oil	35–0
Alkali metal mahogany sulfonate	3–15
Alkali metal resinate	6–0
Alkali metal naphthenate	6–0
Free naphthenic acids	0–0.8
High boiling organic liquid coupling agent	0.4–1.0
Disalicylal propylene diamine	0.2–2.0
Water	1.0–4.0

5. The method in the manufacture of a soluble oil which comprises dissolving rosin in a mineral lubricating oil solution of naphthenic acids and sodium mahogany sulfonate, saponifying the resulting solution with an aqueous caustic soda solution to provide a soap solution in the mineral lubricating oil containing roughly about 50% soap by weight, adjusting the acidity of the mix by adding an excess of naphthenic acids, separately sulfurizing a mineral lubricating oil by heating with free sulfur at a temperature of about 300–340° F. to provide a loosely combined active sulfur content in the oil of about 0.75–3.0% by weight, mixing the sulfurized mineral lubricating oil with the said resulting soap mix in a proportion such that the sulfurized mineral lubricating oil constitutes the major constituent of the mix, and incorporating a high boiling organic liquid coupling agent to produce a soluble oil having extreme pressure properties.

6. The method according to claim 5, wherein the acidity of the soap mix is adjusted by the addition of free naphthenic acids to a neutralization number of 1–3, the water content on the basis of the finished soluble oil is adjusted to 1–4% by weight, and the proportion of sulfurized mineral

lubricating oil on the basis of the finished soluble oil is about 60–70% by weight.

7. An emulsifiable lubricant which is essentially non-corrosive to steel in the presence of water, comprising as the major constituent a sulfurized mineral lubricating oil containing loosely combined active sulfur, an alkali metal soap emulsifier, and about 0.2–2.0% by weight of disalicylal propylene diamine.

8. An emulsifiable lubricant which is essentially non-corrosive to steel in the presence of water, comprising as the major constituent a sulfurized mineral lubricating oil containing loosely combined active sulfur, an alkali metal soap emulsifier, and about 0.2–2.0% by weight based on the lubricant of an aromatic alkylene polyamine selected from the group consisting of benzyl alkylene diamines and salicylal alkylene diamines effective to inhibit said lubricant against steel corrosion in the presence of water.

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