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EXTREME PRESSURE SOLUBLE OIL

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This invention relates to a heavy duty soluble oil composition possessing outstanding extreme pressure properties. More specifically, the invention involves the discovery that a mixture of three extreme pressure additives is an outstanding extreme pressure additive for soluble oils.

In accordance with the present invention, an extreme pressure soluble oil of superior quality is formulated by compounding 60 to 75 weight percent mineral lubricating oil, 1.5 to 2.5 weight percent water, 12 to 20 percent emulsifier and a combination of three different sulfur-containing and chlorine-containing extreme pressure additives, namely (1) chlorinated dibenzyl disulfide, (2) chlorinated paraffin wax and (3) sulfurized sperm oil. The proportions of the three extreme pressure additives is critical in obtaining the desired level of extreme pressure activity in the soluble oil as measured by the SAE load test. The soluble oil compositions of the invention contain the three extreme pressure additives in the following percentages by weight, based on the lubricant:

	Percent by weight
Chlorinated dibenzyl disulfide	4 to 6.0
Chlorinated paraffin wax	3.5 to 5.0
Sulfurized sperm oil	3.5 to 5.0

As a consequence of the trend towards the use of higher machine speeds in cutting operations and the use of soluble oils, that is emulsifiable oils, in these operations where at one time only cutting oils, i. e. non-emulsifiable oils, were used, it has become the practice to add extreme pressure agents to soluble oil formulations. The use of extreme pressure agents has imparted extreme pressure properties to soluble oils thereby remedying their major deficiency. The present invention involves the discovery that a mixture of three specific extreme pressure agents in prescribed amounts is a particularly outstanding additive for soluble oils and that soluble oil formulations obtained by the addition of these three extreme pressure additives in prescribed amounts are characterized by outstanding extreme pressure properties and heat stability.

The mineral lubricating oil used in the formulation of the soluble oil of this invention is preferably a naphthene base distillate oil. Although mixed paraffin-naphthene base distillate oils may be employed, it is desirable to employ a naphthene base distillate fraction because of its better emulsification properties and stability. In general, naphthene base distillate fractions and mixed paraffin-naphthene base distillate fractions having an SUS at 100° F. between 250 and 550 are used in the formulation of the heavy duty soluble oils of this invention.

The water content of the heavy duty soluble oil composition of this invention falls between 1.5 and 3.5 weight percent. A water content of 2 weight percent has been found to be effective in stabilizing the soluble oil composition and in promoting its emulsification with additional quantities of water.

The emulsifiers employed in the formulation of the soluble oil compositions of this invention are the conventional ones employed in soluble oil formulation. Oil-soluble alkali metal petroleum sulfonates, alkali metal naphthenates and alkali metal resinates and mixtures thereof are the emulsifiers usually employed. The sulfonates, naphthenates and resinates are usually employed in the form of their sodium salts because of their lower cost and availability, but other alkali metal salts such as potassium and lithium sulfonates, naphthenates and resinates may also be used.

As is well known, the alkali metal petroleum sulfonates are formed by reaction of concentrated sulfuric acid (90 percent minimum) with a high boiling hydrocarbon fraction in the lube oil range followed by neutralization of the resulting petroleum sulfonate with an alkali metal carbonate or hydroxide.

Alkali metal naphthenates are prepared by neutralization of naphthenic acids isolated from kerosene or higher boiling hydrocarbon fractions. Naphthenic acids isolated from hydrocarbon fractions boiling above about 500° F. are normally used in the formation of alkali metal naphthenates.

Alkali metal resinates are obtained by neutralization of rosin with alkali metal hydroxide or carbonate. Rosin is the residue from distillation of the volatile oil from the oleoresin obtained from pine trees and comprises about 60 to 70 percent of the anhydrides of abietic, sapinic, pimaric, etc. acids. The acid number of the rosin from which the sodium resinate emulsifying agent is derived is not less than about 150.

Mixtures of emulsifying agents, for example a mixture of sodium naphthenate and sodium petroleum sulfonate, a mixture of sodium resinate and sodium petroleum sulfonate, and a mixture of sodium resinate, sodium naphthenate and sodium petroleum sulfonate are effective in imparting the desired emulsion stability to the soluble oil compositions of the invention.

The total emulsifier concentration is between 12 and 20 percent of the total composition with concentrations between 14 and 18 percent usually being employed.

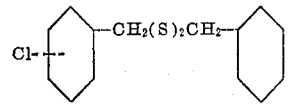
An emulsifying combination which has proven particularly effective comprises an approximately equal part mixture of oil-soluble sodium sulfonate, sodium naphthenate and sodium resinate. A soluble oil composition containing approximately 5 percent of each of these emulsifying agents is an excellent vehicle for the action of the three-component EP mixture of chlorinated dibenzyl disulfide, chlorinated crude scale wax and sulfurized sperm oil.

The heavy duty soluble oils of the invention also advantageously contain minor amounts of coupling agents and bactericides. The coupling agents are usually alkoxy alkanols and more particularly alkoxy ethanols (ethylene glycol monoalkyl ethers) such as ethoxyethanol, also known as Cellosolve. Examples of alkoxy alkanols useful as coupling agents are ethoxyethanol, i-propoxyethanol, n-pentoxyethanol and n-hexoxyethanol. The concentration of the coupling agents is between 0.3 and 1.0 weight percent of the total composition. Butyl Cellosolve, butoxyethanol, in a concentration of 0.6 weight percent has been particularly effective.

Bactericides are also employed in concentrations of the order of 0.3 to 1.0 weight percent of the total soluble oil composition. Halogenated phenols are widely used as soluble oil bactericides and 2,3,4,6-tetrachlorophenol has proven particularly effective in a concentration of about 0.6 weight percent.

Chlorinated dibenzyl disulfide is obtained by chlorination of dibenzyl disulfide and, although not a pure com-

pound, is predominantly monochloro dibenzyl disulfide and can be represented by the following formula:



This product has a chlorine content between 10.4 and 12.5 percent and a sulfur content of 22 to 25 weight percent, which analysis indicates that it is substantially the monochloro compound represented by the foregoing formula.

The concentration of the chlorinated dibenzyl disulfide in the soluble oil is 4 to 6.0 weight percent of the total soluble oil composition; concentrations of 4.5 to 5.5 weight percent are particularly effective. A minimum concentration of 4.0 weight percent is necessary in order to obtain SAE values above 550 at 750 R. P. M. in the SAE EP test.

The chlorinated paraffin wax employed in the present lubricant is one having a high content of combined chlorine, the major proportion of which is in a so-called active state. For example, a preferred material of this character has a total combined chlorine content of about 40–45% with an active chlorine content of about 29–34%. Preferably, the chlorinated paraffin wax contains a small proportion of an oil-soluble corrosion inhibitor of the type disclosed in U. S. Patent No. 2,298,638, which functions to neutralize the effect of any decomposition of the chlorinated paraffin wax with the release of free chlorine. The chlorinated paraffin wax used hereafter contains a small amount of phenoxy propylene oxide as a corrosion inhibitor of this type.

The concentration of the chlorinated paraffin wax is 3.5 to 5.0 weight percent of the soluble oil composition, with concentrations of about 4.0 weight percent normally being employed.

The sulfurized sperm oil composition employed in the present lubricant may be prepared by sulfurizing sperm oil with about 8–15% of sulfur at 350–400° F. for about 1–3 hours. The resulting sulfurized product contains about 7–13% of combined sulfur in a form which renders the product non-corrosive in the copper strip corrosion test and yet is sufficiently active to provide the required chemical reaction at elevated temperatures which is responsible for the extreme pressure properties thereof. Typical tests on sulfurized sperm oil, which is mainly sulfurized cetyl oleate, are the following:

Gravity, ° API	14.5–16.0
SUS viscosity at 210° F	190–230
Sulfur, wt. percent	9–11
Sap. No	140–155

The concentration of the sulfurized sperm oil in the soluble oil composition of the invention falls between 3.5 and 5.0 weight percent.

A heavy duty soluble oil formulation which gave excellent results in the screening tests, namely the SAE EP test and the heat stability test, as will be demonstrated hereafter, and which has given excellent results in field trial, contained chlorinated dibenzyl disulfide, chlorinated crude scale wax and sulfurized sperm oil in a ratio of 4.8:4.0:4.0, in which ratio the amounts designate the concentration in weight percent of the respective ingredients in the finished soluble oil formulation.

The SAE load test was used to determine the extreme pressure properties of the soluble oils. When evaluating emulsions of the soluble oils, for example an emulsion comprising 10 parts of water and 1 part soluble oil, the SAE load test was modified slightly in that during the test a constant stream of the emulsion was directed at the test cup until it scored or the capacity of the machine was exceeded. This procedure differs from the standard test employed for the soluble oil per se wherein the test sample is placed in the boat underneath the test cup prior to applying the load.

The heat stability test, which correlates well with storage stability on the basis of field experience, consists of holding soluble oil samples at 160° F. and observing the appearance and odor of the product under test. When a change in either appearance or odor of the product under test is noted, the time is recorded and the results are reported in number of hours to fail. If the product under test displayed no change in appearance or odor after 10 days (240 hours) of storage at 160° F., it was deemed to possess excellent heat stability and the test was discontinued. Exposure to this test results in accelerated odor formation and green discoloration due to generation of H_2S and comparable to that which develops in storage on standing.

In the following table there is shown the outstanding extreme pressure properties and heat stability of the soluble oil formulation of this invention containing a mixture of chlorinated dibenzyl disulfide, chlorinated paraffin wax, and sulfurized sperm oil as an extreme pressure additive mixture. The data in the table also clearly show the specificity of the mixture of three extreme pressure agents in obtaining the desired level of extreme pressure properties and heat stability since other formulations containing mixtures of closely related extreme pressure agents failed one or both of the screening tests shown in the table.

The base oil to which various EP agents were added in the formulation of the composition shown in Table I comprised a mineral oil consisting essentially of a naphthene base distillate oil having an SUS viscosity at 100° F. of about 390, 4.9 percent sodium resinate, 4.9 percent sodium naphthenate, 5.2 percent sodium petroleum sulfonate, 0.6 percent butyl Cellosolve, 0.6 percent 2,3,4,6-tetrachlorophenol and 1.8 percent water. The concentrations of the emulsifying agents, bactericide, butyl Cellosolve and water remain constant in the various experimental formulations while the naphthene base mineral oil concentration was adjusted to compensate for the concentration of extreme pressure additives in the amounts shown in the table.

Table I

Run No.	Base Oil Containing—	SAE Load Test, 750 R. P. M.	Heat Test at 160° F., Hrs. to Fail
1	4% dibenzyl disulfide and 6% pentachloro naphthalene.	252	240+
2	4% dibenzyl disulfide and 6% chlorinated paraffin wax.	190	240+
3	4% dibenzyl disulfide and 6% sulfochlorinated sperm oil.	183	168+
4	4% dibenzyl disulfide and 4% chlorinated paraffin wax.	237	240+
5	4% dibenzyl disulfide and 4% sulfochlorinated sperm oil.	166	168+
6	4% dibenzyl disulfide and 4% benzene dichloride.	170	168+
7	4.9% chlorinated dibenzyl disulfide and 4% chlorinated paraffin wax.	158	48
8	4% dibenzyl disulfide, 4% chlorinated paraffin wax and 4% sulfurized sperm oil.	480	240
9	4.8% chlorinated dibenzyl disulfide, 4% chlorinated paraffin wax and 4% sulfurized sperm oil.	550+	240

The soluble oil composition represented by run No. 9, containing 4.8% chlorinated dibenzyl disulfide, 4% chlorinated paraffin wax and 4% sulfurized sperm oil, consistently gave values of 550+ in the SAE load test at 750 R. P. M. and of 240+ in the heat stability test at 160° F. None of the other compositions shown in Table I was able to approach the effectiveness of this combination of additives in the SAE load test.

In Table II there is shown a comparison of a soluble oil formulation of this invention containing a mixture of chlorinated dibenzyl disulfide, chlorinated paraffin wax and sulfurized sperm oil as an EP agent with a soluble

oil product which had substantial commercial use prior to its replacement with the soluble oil composition of this invention.

The soluble oil composition of the invention, identified as Soluble Oil A in Table II, comprised 69.2% of a mineral oil consisting essentially of a naphthene base distillate oil having an SUS viscosity at 100° F. of about 390, 4.9 percent sodium resinate, 4.9% sodium naphthenate, 5.2% sodium sulfonate, 0.6% butyl Cellosolve, 0.6% 2,3,4,6-tetrachlorophenol, 1.8% water, 4.8% chlorinated dibenzyl disulfide, 4.0% chlorinated paraffin wax and 4.0% sulfurized sperm oil. The former commercial product, identified in the table as Soluble Oil B, comprised 14.6% of a mineral oil consisting essentially of a naphthene base distillate oil having an SUS viscosity at 100° F. of about 70, 66.5% sulfurized naphthene base distillate containing 1.2 weight percent sulfur and obtained by sulfurization of a naphthene base distillate having an SUS viscosity at 100° F. of 750 with 1 weight percent sulfur at a temperature of 300 to 350° F., 4.9% sodium resinate, 4.9% sodium naphthenate, 5.2% sodium sulfonate, 0.6% butyl Cellosolve, 0.6% 2,3,4,6-tetrachlorophenol, 2.3% water and 0.4% N'-disalicylidene diaminopropane.

Table II

Avg. Tests	Soluble Oil A	Soluble Oil B
Emulsion Area	Large	OK
Rusting Test:		
No Rust-Rust	45-50	25-30
MCI, No Rust-Rust	75-80	40-45
Corr.:		
1020 Steel at 150° F	OK	OK
10:1 emulsion	OK	OK
SAE:		
750 R. P. M	550+	258
500 R. P. M. (10:1 dilution)	140	114
Heat Stability Test at 160° F.,[1] Hrs. to Fail	240+	16

[1] Soluble Oil A was also stable at 180° F. for 240+ hrs.

Soluble Oil A, in which the EP properties are derived from the use of a mixture of chlorinated dibenzyl disulfide, chlorinated paraffin wax and sulfurized sperm oil in the amounts prescribed in this invention, is significantly superior in (1) color and odor stability as measured by the heat stability test, (2) extreme pressure characteristics as measured by the SAE load test and (3) anti-staining properties as measured by the rusting test to Soluble Oil B, in which the extreme pressure properties are obtained by sulfurization of the mineral lubricating base oil.

The rusting test employed in Table II is specifically designed to evaluate the rust protection afforded by soluble oils and involves determination of what dilution of a soluble oil in synthetic hard water will cause the rusting of cast iron. The procedure involves placing portions of emulsions formed from the soluble oil and varying amounts of synthetic hard water on a polished cast iron plate 11" x 5½" x ½" which is cross hatched into 162 equal 9/16" squares. Drops of emulsions ranging from a 10:1 dilution to a 90:1 dilution in increments of 5 are placed on different squares of the polished cast iron plate. The plate containing the various dilutions is allowed to stand overnight in an area where there is adequate ventilation, under which conditions the emulsion drops are evaporated in 1 to 2 hours. The squares are examined for signs of rust and the highest dilution showing no rust whatever is noted and reported as "No rust" and the lowest dilution showing rust is noted and reported as the "Rust" dilution. The synthetic hard water contains 125 P. P. M. hardness and is prepared by dissolving 2.77 g. of anhydrous calcium chloride and 5 gallons of distilled water and adjusting the pH to 6.5 to 7.5 by the addition of 10 percent of H_2SO_4 or 10 percent $NaHCO_3$. The test is often repeated with a polished malleable cast iron plate substituted for the polished cast iron plate. In the data reported in Table II, the results with the malleable cast iron plate are identified as MCI. The data in Table II indicate that the soluble oil of the invention, Soluble Oil A, gave no rust at 45 to 1 dilution and some rust at 50 to 1 dilution with polished cast iron plate; with malleable cast iron plate, no rust was obtained with dilutions up to 75 to 1 but rust started at a dilution of 80 to 1.

Field evaluation of the soluble oil composition of this invention, represented by run No. 9, has confirmed the excellent results obtained in the screening test. Excellent tool life and cutting properties have been obtained with this product.

In one commercial installation a product having the same composition as Soluble Oil A of Table II was used for the turning of bar stocks of stainless steel with excellent results, as evidenced by the fact that an expensive bar cleaning operation was eliminated by its use. In another location the use of the soluble oil of the invention in a vertical saw cutting operation gave such good results that the product is currently being used in all broaching operations. In a third location, evaluation of the soluble oil of the invention in a broaching operation resulted in improved tool life and finish; the product of the invention in a 20:1 dilution ratio gave results better than the formerly used product in a 15:1 dilution ratio.

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 soluble oil composition suitable for heavy duty metal cutting operations comprising mineral lubricating oil as the major constituent, oil-soluble emulsifying agents in an amount sufficient to cause formation of oil-in-water emulsions on mixing the soluble oils with water, and the following additives in percent by weight based on the soluble oil:

	Percent by wt.
Chlorinated dibenzyl disulfide	4 to 6
Chlorinated paraffin wax	3.5 to 5
Sulfurized sperm oil	3.5 to 5

2. A soluble oil composition according to claim 1 in which said mineral oil is selected from the group consisting of naphthene base distillate oil, mixed paraffin-naphthene base distillate oils and mixtures thereof.

3. A soluble oil composition suitable for heavy duty metal cutting operations comprising mainly the following constituents in percent by weight based on the soluble oil:

	Percent by wt.
Mineral lubricating oil	60 to 75
Oil-soluble emulsifiers	12 to 20
Water	1.5 to 3.5
Chlorinated dibenzyl disulfide	4 to 6
Chlorinated paraffin wax	3.5 to 5
Sulfurized sperm oil	3.5 to 5

4. A soluble oil composition suitable for heavy duty metal cutting operations comprising mainly the following constituents in percent by weight based on the soluble oil:

	Percent by wt.
Naphthene base distillate oil	60 to 75
Emulsifier selected from the group consisting of alkali metal petroleum sulfonates, alkali metal naphthenates, alkali metal resinates and mixtures thereof	12 to 20
Water	1.5 to 3.5
Bactericide	0.3 to 1.0
Alkoxy ethanol	0.3 to 1.0
Chlorinated dibenzyl disulfide	4 to 6
Chlorinated paraffin wax	3.5 to 5
Sulfurized sperm oil	3.5 to 5

5. A soluble oil composition suitable for heavy duty metal cutting opeartions comprising mainly the following

constituents in percent by weight based on the soluble oil:

	Percent by wt.
Mineral oil consisting essentially of naphthene base distillate oil having an SUS at 100° F. of 390	69.2
Sodium petroleum sulfonate	5.2
Sodium resinate	4.9
Sodium naphthenate	4.9
Butoxyethanol	0.6
2,3,4,6-tetrachlorophenol	0.6
Water	1.8

Chlorinated dibenzyl disulfide	4.8
Chlorinated paraffin wax	4.0
Sulfurized sperm oil	4.0

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