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SOLUBLE OIL BASE

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This invention relates to soluble oil compositions having excellent rust and/or corrosion inhibiting properties. More particularly, this invention pertains to an all-purpose soluble oil composition which is applicable as a rust inhibitor for ferrous metals, and/or as a coolant and lubricant for metal working of ferrous and non-ferrous metals.

Metallic surfaces exposed to moisture, corrosive fluids and the like are readily attacked and rust or corrode. Such conditions are usually encountered when transporting metal articles over bodies of water, or when storing them or exposing them for long periods of time to highly humid conditions. Metals which are quenched or immersed in or sprayed with aqueous mediums, particularly electrolytic solutions, become susceptible to rusting and/or corrosion due to the strong affinity and adherence of the moisture for the metal surface. Corrosion of metals is also caused by acids formed during combustion of halides in ethyl fluids or decomposition of lubricants during operation of internal combustion engines and the like. Handling of metals also causes corrosion and is generally referred to as fingerprint corrosion. At elevated temperatures the above conditions become aggravated and corrosion activity is enhanced due to the increased chemical activity of moisture and corrosive fluids towards the metal.

Various substances have been tried for preventing rusting and/or corrosion of metals. In the majority of cases such compositions comprise oleaginous bases such as mineral lubricating oil, fatty oils, greases and the like containing minor amounts of corrosion inhibitors such as natural or synthetic resins or waxes, cellulose esters or ethers, wool fat, paraffin wax, resinates, preferably the barium, magnesium and aluminum resinates; metal salts of polyalkyl diphenol sulfides; alkylene polycarboxylic acids, i. e. alkylene succinic acid; substituted fatty acids, i. e. mercapto stearic acid and the like. In the majority of cases such compositions have proved to be of little value as rust and/or corrosion inhibitors due to their relative inability to displace moisture and other adhering contaminants from metal surfaces as well as their inability to inhibit decomposition or deterioration of the medium in which they are dispersed, especially at elevated temperatures and their short active life.

It has now been discovered that soluble oils of the type which will hereinafter be disclosed are superior to any known aqueous and non-aqueous rust inhibiting compositions. The active components of compositions of this invention possess a greater affinity for metals than does water and readily displace it from the metal surface. In addition they possess excellent spreading and wetting characteristics forming on ferrous and non-ferrous surfaces a continuous strong adhering protective film which is impervious to moisture and/or corrosive fluids and is not easily ruptured. Other components of this composition possess the property of readily adsorbing displaced moisture forming stable emulsions and thereby removing moisture as a future potential corrosion inhibitor in event the protective film is ruptured. Certain ingredients of this invention possess the property of neutralizing acidic materials as they are formed thereby inactivating them and rendering them harmless.

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In order that the active rust inhibiting constituents of this invention exert their maximum influence and operate at maximum efficiency they must be blended in such proportions as to possess good emulsifiability, good solubility in the base stock in which they are dispersed and resist oxidation. By coupling or bridging the oil-soluble ingredients and the water-soluble ingredients with blends of materials of graduated solubility which range from compounds miscible with water at one end to compounds miscible with oil at the other end, a stable emulsion can be obtained, the active components of which are free to function as desired.

It is an object of this invention to provide a new rust and/or corrosion inhibiting compositing when applied over metal surfaces. Another object is to provide soluble oil compositions having excellent water displacing and rustproofing properties. Still another object is to provide soluble oil compositions which inhibit rusting of metals due to handling or when in contact with corrosive fluids. A further object is to provide soluble rust inhibiting compositions which are resistant to adverse conditions of temperature. A still further object is to provide soluble oil compositions for inhibiting rusting of metals which can be readily applied and easily removed. Still another object is to provide rust inhibiting soluble oils suitable for metal cutting, working and the like.

These and other objects are accomplished according to the present invention by preparing a soluble oil containing highly polar compounds at least one of which is an oil-soluble alkali metal salt of petroleum sulfonic acid and another is a water-soluble salt of a hydroxy fatty acid having at least 10 carbon atoms and preferably between about 16 to 18 carbon atoms. These salts are selected so that they are mutually miscible with each other, and are bridged with specific coupling and stabilizing agents so as to produce a stable, non-corrosive emulsion which is readily miscible with liquid petroleum hydrocarbon. The sulfonate constitutes between about 40% and about 65% and the water-soluble salt of a hydroxy fatty acid constitutes between about 10% and about 25% by weight of the composition.

Suitable sulfonates, particularly the sodium

salts of oil-soluble petroleum sulfonic acids are obtained by treating suitable petroleum hydrocarbon fractions with sulfuric acid. Petroleum fractions which can thus be treated to obtain desired sulfonates are gasoline, naphtha, kerosene, furnace oil, neutral oil, turbine oil and generally mineral oils which contain around about 5% or higher aromatic constituents. For example, a turbine oil having a Saybolt Universal viscosity at 100° F. of from about 400 to 540 seconds can be treated with fuming sulfuric acid, preferably in small increments. After a calculated amount of sulfuric acid has been added to the oil, the sludge which forms is removed and the acid-treated oil containing dissolved oil-soluble sulfonic acid is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is removed from the mixture and the sodium salts of petroleum sulfonic acid extracted with alcohol. The alcohol layer containing the sulfonates can be removed by distillation or by any other suitable means.

Modifications to the above procedure can be made by removing acid sludge after each added increment of sulfuric acid, rather than removing it after the entire required amount of acid has been added. Also the sulfonic acid can be removed before neutralization rather than after as indicated above. If this is done, it is preferable to give the acid-treated oil a clay treatment so as to remove inorganic esters of sulfuric acid and other impurities so as to prevent formation of inorganic salts. Clays which are particularly suitable are highly absorbent clays such as Attapulgus clay, floridin, bentonite, bauxite, fuller's earth, etc. Still another modification in preparing pure oil-soluble sulfonates is to add to the sludge free acid-treated oil a solvent such as benzol, carbon tetrachloride and the like and neutralizing said mixture with a caustic solution. The spent caustic solution is removed and the solvent distilled off, leaving a substantially pure sulfonate in an oil mixture. The product can be air blown and dehydrated to remove impurities. Sulfonates prepared from turbine oils by the above means generally have a molecular weight of from between about 425 to 600. Sulfonates which have a molecular weight between about 540 to 570 are preferred as additives in this invention and they usually contain from about 45% to about 70% of sodium sulfonate; about 20% to 40% mineral oil; about 7% to 10% water and from 2% to 5% impurities. Other salts which can be used to produce the sulfonates are lithium, potassium, cesium and the like.

The water-soluble salts of hydroxy fatty acids having at least 10 carbon atoms are obtained by saponification of hydroxy saturated and unsaturated fatty acids such as dimethyl hydroxy caprylic acid, dimethyl hydroxy capric acid, hydroxy physetoleic acid, ricinoleic acid, ricinelaidic acid, hydroxy stearic acid, linusic acid, sativic acid and the like with an alkali metal such as sodium, potassium or by neutralizing said acids with ammonium; alkyl and alkylol amines, e. g. ethyl and diethyl amine, propyl and isopropyl amine, butyl and isobutyl amine, diethylaminopropylamine, ethanolamine, ethyl and diethyl ethanol amine, butyl ethanol amine, dibutylaminoethanol and the like. Among the preferred salts are ammonium and sodium ricinoleate.

To stabilize mixtures of oil soluble alkali petroleum sulfonates and water soluble salts of hydroxy fatty acids coupling agents are added in

amounts generally not exceeding 10% and preferably are kept in the range of from 4 to 10% by weight. The preferred coupling agents are selected from the group consisting of alkylene glycol, glycol mono-alkyl ethers, diglycol mono-alkyl ethers and aliphatic alcohols. Specifically the following coupling agents can be used:

Ethylene glycol mono-ethyl ether
Ethylene glycol mono-propyl ether
Ethylene glycol mono-n-butyl ether
Ethylene glycol mono-isobutyl ether
Ethylene glycol mono-tertianylbutyl ether
Ethylene glycol mono-hexyl ether
Propylene glycol mono-ethyl ether, etc.
Diethylene glycol mono-methyl, ethyl, n and isopropyl ethers,
Diethylene glycol mono-butyl ether
Diethylene glycol mono-decyl ether
Dipropylene glycol mono-ethyl ether
Dipropylene glycol mono-isopropyl ether
Dipropylene glycol mono-isoamyl ether
Dipropylene glycol mono-heptyl ether
Ethylene-propylene glycol mono-ethyl ether
Ethylene-isobutylene mono-isopropyl ether, etc.
Ethylene glycol, propylene glycol, hexylene glycol, etc., isopropanol, butanol, etc. The coupling agents can be used alone or in mixtures.

To aid in forming a stable emulsion minor amounts of from 1% to 5% by weight of glycerin can be added to the mixture. The addition of glycerin does not only facilitate emulsifiability but prevents separation especially at low temperatures.

To improve the rust inhibiting and lubricating properties of compositions of this invention, particularly when they are used as metal working lubricants, a minor amount of fixed fatty oils and/or waxes preferably not exceeding 10% by weight and more particularly when kept in the range of from about 4 to 10% can be admixed. Fixed fatty materials which can be used are animal, vegetable and marine oil and/or waxes and include neat's-foot oil, horse fat, beef tallow, mutton tallow, degras, lard oil; olive oil, peanut oil, castor oil, cocoanut oil, palm oil, Japan wax, cottonseed oil, kapok oil, sesame oil, corn oil, colza oil, sperm oil, seat oil, whale oil, dolphin oil, menhaden oil, sardine oil, codliver oil, etc.

When fixed fatty oils are added it is advisable to add small amounts of a germicidal agent so as to inhibit bacterial growth and fermentation. Emulsions containing fixed oils are very susceptible to deterioration especially when used at elevated temperatures for long periods of time. Such emulsions develop an extremely strong, foul and undesirable odor rendering them practically useless. Bacterial growths also cause metal discoloration and are a constant danger to the health of the user. The addition of a germicidal agent such as Formalin (aqueous solution of approximately 40% formaldehyde) or phenolic compounds e. g. phenol, chlor para phenyl phenol, o-phenyl phenol and the like are very beneficial in not only inhibiting bacterial growth but in preventing discoloration of metals and deterioration of emulsions. The amount of germicidal agent used generally does not exceed 5% by weight.

Soluble oils of this invention can be made simply and efficiently, requiring no special technique or equipment. To obtain a stable product, however, care should be taken to adhere to certain proportional limits of each ingredient

used to make up the soluble oil. The product can be made by first mixing the water soluble ingredients together and then slowly adding the oil-soluble ingredients under constant agitation. No external heat is required because of the heat of neutralization and reaction although if desired the emulsion can be made using heat to facilitate the process. For example, calculated amounts of water, sodium hydroxide solution, Formalin, glycerin and ethylene glycol ethyl ether are admixed and agitated in a suitable vessel. A required amount of ricinoleic acid is slowly added and the mixture agitated until a soap of sodium ricinoleate forms in the solution. To this mixture is added, sodium petroleum sulfonate, and if desired, a small amount of a fatty oil such as extra winter strained lard oil and the entire mixture agitated until a homogeneous mass is obtained.

A specific example henceforth referred to as composition A of a soluble oil obtained by the above method comprised:

	Percent weight
Water	11.8
Sodium hydroxide	2.4
Formalin (approx. 40% HCHO)	2.2
Glycerin	6.1
Ethylene glycol ethyl ether	5.8
Ricinoleic acid	16.6
Sodium sulfonate (100%)	46.1
Extra winter strained lard oil	9.0

Soluble oils of this invention can be used per se or preferably blended with a suitable petroleum base in amounts varying from 1 to 30% and preferably between about 10 to 20% by weight depending upon the petroleum base and intended use of the composition. Petroleum products which can be used as bases are: kerosene, mineral seal oil, gas oil, petroleum naphtha cuts, mineral spirits, aromatic solvents, mineral lubricating oil, petroleum waxes and the like. The additive mixture can be admixed with a suitable petroleum base by heating the base to around about 100° F. and slowly adding the additive mixture under constant agitation until a homogeneous mass is obtained. A general formula of base compositions of this invention contain the following components by weight:

	Per cent
Petroleum base (mineral lubricating oil)	70–90
Additive mixture of this invention, i. e. composition A	1–30
Water	0.5–4

Base compositions as noted may be diluted with a major amount of water or other aqueous medium in order to obtain desired rustproofing and metal working lubricants. Excellent cutting emulsions are obtained by using about 25% of the base and diluting it with about 75% water. If desired, in some cases the base may be diluted with as much as 100 to 200 parts of water.

The efficiency of compositions of this invention as rust inhibitors and metal working lubricants can best be illustrated by comparative test with the best available compositions used for the same purpose.

Humidity test

Sand blasted panels of mild steel were dipped five times during a period of 30 seconds into aqueous emulsion of test compositions as noted in the following table. The panels were then allowed to remain vertically to drain for 20 hours under ordinary room temperature. The panels were then placed in a humidifier chamber in which the temperature was maintained at 100° F. and the humidity at 100° F. The time for the panels to develop rust was observed and recorded as the resistance life of the composition.

	Composition	Hours to Initially Rust
1	Mineral lubricating oil+10% of Composition X [1].	10 minutes.
2	Mineral lubricating oil+10% of Composition A.	100 hours.

[1] Composition X consists of 76% mineral oil, 20% sodium sulfonate, 4% water, and 0.5% o-phenyl phenol.

Shed exposure test

Polished steel panels were dipped in aqueous emulsions of test compositions specified in the following table, for 10 seconds and exposed to the atmosphere for 5 days. The panels were then inspected for signs of rust.

Amount	Composition A	Composition X	Composition Y [1]	Composition Z [2]
5% aqueous emulsion	No Rust	Heavy Rust	Very Heavy Rust.	Very Heavy Rust.
3% aqueous emulsion	Light Rust which was very thin and easily removed by wiping.	do	do	Do.
1% aqueous emulsion	do	do	do	Do.

[1] Composition Y comprises: 70.5% mineral oil, 27.5% sodium sulfonate, 20% water and 0.5% o-phenyl phenol.
[2] Composition Z comprises: 75% mineral oil and 25% of a 50–50 mixture of sodium sulfonate and sodium rosin soap.

Compositions of this invention make excellent cutting fluids because of their outstanding cooling and lubricating properties. In metal working operations such as cutting, reaming, drilling, threading, drawing, etc., extremely high temperatures and pressures are developed causing failure of the cutting or working tool or undesired finish of work piece or both. Machining failure is generally due to build-up microscopic metal particles formed during machining and which weld and build up on the tool surface. This build-up edge due to great compressibility forces exerted on the tool break off, damaging the tool and work piece.

Effective coolants and lubricants for metal working must possess a high degree of chemical reactivity with the machined metal surface so as to form thereon a protective film capable of withstanding extreme pressures. They must also be free flowing so as to readily enter the crack formed between the tool and workpiece and act as a lubricant.

To illustrate the remarkable friction reducing properties of soluble oils under consideration possess, these oils were tested in a multiple four-ball machine similar in principle to the Boerlage apparatus described in the magazine, Engineering, vol. 136, July 14, 1933, and compared with other products. This apparatus comprises four steel balls arranged in pyramid formation. The top ball is rotated by spindles against the three bottom balls which are clamped in a stationary ball holder. The balls are immersed in the test composition. Tests were run at 700 R. P. M. under 14.1 kg. load at 30° C. The diameters of

the wear scars worn on the three balls forming the base of the pyramid were then measured and the average taken as the true indication of wear.

The results were as follows:

Table

	Scar diameter (mm.)
1. 10% soluble oil blend of composition A	0.49
2. 10% soluble oil blend of composition X	0.63
3. Aqueous emulsion of 10% of a soluble oil blend of composition A in 90% water	0.60
4. Aqueous emulsion of 10% of a soluble oil blend of composition X in 90% water	0.87
5. Distilled water	0.96

Other additives can be added to compositions of this invention in order to improve their performance. Thus extreme pressure additives such as sulfurized and sulfurized-halogenated olefinic hydrocarbons and/or fatty oil, e. g. sulfurized sperm oil, sulfurized lard oil; sulfonated castor oil can be used. Also oiliness agents such as oleic and stearic acids, soaps, etc; anti-foaming agents such as dicetyl silicone; anti-oxidants such as phenolic and amine compounds and the like can be added to compositions of this invention generally in amounts of around about 0.5 to 5% by weight.

Compositions of this invention can be easily modified to meet required conditions for combating rust. Thus in the case of protection of furnished metal articles the additive agents of this invention can be dispersed in a light hydrocarbon which evaporates readily and leaves behind a protective coating. Where metals are exposed to heavy rains and highly humid conditions they can be immersed in compositions of this invention having as a base a heavy oil or wax which can be removed by flushing or wiping.

Many modifications and variations of this invention as hereinbefore set forth can be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as indicated in the appended claims.

I claim as my invention:

1. An oil base soluble in an aqueous medium adapted for use as a rust inhibitor and metal working lubricant containing the following constituents in the following proportions:

	Percent weight
Water	11.8
Sodium hydroxide	2.4
Formalin (approx. 40% HCHO)	2.2
Glycerin	6.1
Ethylene glycol ethyl ether	5.8
Ricinoleic acid	16.6
Sodium sulfonate (100%)	46.1
Extra winter strained lard oil	9.0

said constituents being blended with from 70% to 90% of a mineral lubricating oil.

2. A lubricating emulsion comprising an aqueous medium having solubilized therein a minor amount sufficient to impart rust-inhibiting properties, a composition which consists essentially of 70% to 90% mineral oil in combination with from 30% to 10% of a base comprising 40 to 65% of an oil-soluble alkali metal salt of petroleum sulfonic acid, substantially 10 to 25% of a water-soluble salt of a hydroxy fatty acid having at least 10 carbon atoms, from 4% to 10% of a stabilizing agent from the group consisting of aliphatic alcohol, di-glycol mono-alkyl ether, and glycol mono-alkyl ether and the balance being water.

3. A lubricating emulsion comprising an aqueous medium having solubilized therein a minor amount sufficient to impart rust-inhibiting properties, a composition which consists essentially of 70% to 90% mineral oil in combination with from 30% to 10% of a base comprising 40% to 65% of an oil-soluble sodium salt of petroleum sulfonic acid, substantially 10% to 25% of sodium ricinoleate, from 4% to 10% of a mixture of ethylene glycol mono-ethyl ether, and glycerin and the balance being water.

4. A lubricating emulsion comprising an aqueous medium having solubilized therein a minor amount sufficient to impart rust-inhibiting properties, a composition which consists essentially of 70% to 90% mineral oil in combination with from 30% to 10% of a base comprising 40% to 65% of an oil-soluble sodium salt of petroleum sulfonic acid, substantially 10% to 25% of ammonium ricinoleate, from 4% to 10% of a mixture of ethylene glycol mono-ethyl ether, and glycerin and the balance being Formalin.

5. A lubricating emulsion comprising an aqueous medium having solubilized therein a minor amount sufficient to impart rust-inhibiting properties, a composition which consists essentially of 70% to 90% mineral oil in combination with from 30% to 10% of a base comprising 40% to 65% of an oil-soluble sodium salt of petroleum sulfonic acid, substantially 10% to 25% of sodium hydroxy stearate, from 4% to 10% of a mixture of ethylene glycol mono-ethyl ether, and glycerin and the balance being Formalin.

6. A lubricating emulsion comprising an aqueous medium having solubilized therein a minor amount of from 1% to 30% of a composition which consists essentially of 90% mineral oil in combination with about 10% of a base comprising 65% of an oil-soluble sodium salt of petroleum sulfonic acid, substantially 25% of a water-soluble sodium salt of a hydroxy fatty acid having at least 10 carbon atoms, from 4% to 10% of a stabilizing agent from the group consisting of aliphatic alcohol, di-glycol mono-alkyl ether, and glycol mono-alkyl ether and the balance being water.

7. An oil base soluble in an aqueous medium adapted for use as a rust inhibitor and metal-working lubricant containing the following constituents in the following approximate proportions:

	Percent weight
Water	11.8
Sodium hydroxide	2.4
Formalin (approx. 40% HCHO)	2.2
Glycerin	6.1
Ethylene glycol ethyl ether	5.8
Hydroxy aliphatic hydrocarbon carboxylic acid having 18 carbon atoms and not more than one double bond in the molecule	16.6
Sodium petroleum sulfonate (oil-soluble)	46.1
Extra winter strained lard oil	9.0

10% to 30% of the composite of said constituents being blended with from 70% to 90% of a liquid petroleum oil base.

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