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SOLUBLE METALWORKING LUBRICANT

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This invention relates to improved lubricating compositions and more particularly to emulsifiable lubricating compositions adapted for cooling and lubricating of surfaces subjected to high speeds, high temperatures, extreme pressures and the like, such as encountered in various metal fabrication operations.

Lubricants suitable for use in metal fabrication such as in lathe work, cutting, drilling, reaming, broaching, drawing and the like must effectively cool and lubricate both the tool and worked metal. During such operations an enormous amount of heat is generated at the tool and work piece interface which must be quickly dissipated therefrom in order to prevent damage to either the tool or work piece or both. This can only be accomplished by flooding the tool and work piece with a fluid having a high capacity for heat adsorption. The second function of such fluids, that of lubrication, is essential in reducing friction between contacting metals, thus preventing wear, scoring and even welding of contacting metal parts. Effective lubrication of the tool and work piece during metal cutting and the like reduces the tendency of build-up formations on the tools which generally account for rough surface finishes, inaccurate cutting dimension and even tool failure. Cutting fluids which adequately perform the functions discussed increase tool life, increase the speed of such operations, improve the surface finish of the work piece, decrease power consumption by efficient lubrication and the like.

Countless compositions have been compounded for aiding in cooling and lubricating during metal fabrication such as cutting and the like. Where a cooling effect is most desired water is most suitable because of its high capacity to adsorb heat. However water has a serious drawback in that it causes corrosion and is an exceedingly poor lubricant. Although addition of corrosion inhibitors to water can aid in overcoming its corrosion tendencies, the composition still remains a poor lubricant, thus rendering substantially useless as a cutting fluid especially under stringent operating conditions. Straight hydrocarbon oils although they aid lubrication to some extent are relatively poor coolants and are incapable of acting as effective lubricants under extreme pressure conditions and high temperatures. To some extent the addition to straight hydrocarbon oils of fixed fatty oils or sulfurized and/or halogenated fatty oils or other such treated materials, aids lubrication under cutting conditions, by increasing the oiliness and film

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strength of the lubricant. However the presence of such materials in a hydrocarbon oil does not improve its cooling properties and frequently is the cause of corrosion and staining the work piece. Fixed oils also have a tendency of becoming rancid, developing obnoxious odors thereby rendering them useless. Highly halogenated additives as well as mineral oil frequently cause skin irritation resulting at times in serious cases of dermatitis. Water in oil or oil in water emulsions containing extreme pressure additives designed to utilize combined beneficial effects of water and oil, fortified by extreme pressure additives have met with little success. Such emulsions are generally unstable, having a tendency to thicken due to evaporation of water, become gummy, causing clogging of conduit lines and sticking of movable machine parts.

It is an object of this invention to produce a cutting fluid having excellent cooling and lubricating properties. Another object of this invention is to produce a non-corrosive aqueous cutting emulsion. Still another object of this invention is to produce a stable, non-corrosive, aqueous cutting composition free of ingredients of an infectious nature. Furthermore it is an object of this invention to produce a multi-functional metal working lubricant suitable for use at high speeds, pressures and temperatures.

The above and other objects may be attained, in accordance with the present invention, by adding to water or any aqueous composition, a minor amount, generally less than 5% by weight (although it may be from a fraction of one percent to 10% or higher), of a reaction product prepared by forming adducts from an organic compound having at least one unsaturated linkage between two carbon atoms, and hydrogen sulfide or mercaptan, and thereafter separating from the mixture of compounds present in such adduct, that fraction thereof volatilizing at relatively low temperatures, thereby isolating the desired reaction product for use in aqueous compositions suitable for metal cutting and the like.

The unsaturated organic compounds from which the reaction products of this invention may be prepared possess at least one unsaturated linkage between two aliphatic carbon atoms regardless of the character of the compound embracing such a linkage. The unsaturated hydrocarbons such as the olefins (which term is intended to include mono-olefins, di-olefins and polymers thereof) are particularly contemplated. Examples of unsaturated hydrocarbons are: ethylene, propylene, 1-butene, 2-butene, isobutylene, the

amylenes, 1-hexene, 2-hexene, 4-methyl-1-pentene, 4-methyl-2-pentene, 4,4-dimethyl-1-pentene, 1-octene, 1-decene, 1-cetene, styrene, cyclohexene, 3-methyl-cyclohexene, 1,4-diphenyl-2-butene, 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, acetylene, methylvinylacetylene, octylacetylene, phenylacetylene, and their homologs and analogs. When mono-olefins are used, those having a relatively high molecular weight are preferred.

The unsaturated hydrocarbons of the above-defined class may also have one or more of their hydrogen atoms substituted by suitable organic and/or inorganic substituents, which may include substituents such as alkoxy, alkenoxy, aryloxy, alkyloxy, aralkyloxy, alkylimido, etc.

The reaction products prepared according to the present invention are especially versatile if the unsaturated compound has a terminal aliphatic unsaturated linkage. The unsaturated ethers, such as diallyl ether and divinyl ether, meet this latter requirement and are a preferred class of substances useful in the preparation of the lubricants of the present invention. One group of such unsaturated ethers comprises the aliphatic oxyethers in which only one of the aliphatic radicals attached to the ether oxygen atom contains an unsaturated linkage. Examples of such ethers are ethyl vinyl ether, ethyl propenyl ether, methyl isopropenyl ether, ethyl isopropenyl ether, methylallyl ether, ethyl allyl ether, n-propyl allyl ether, isopropyl allyl ether, 4-ethoxy-1-butene, 6-ethoxy-1-hexene, ethyl propargyl ether, etc. and their homologs and analogs. The above unsaturated ethers and their homologs may be substituted by straight-chain, cyclic and/or heterocyclic radicals, as well as by halogens.

Another group of suitable unsaturated ethers which may be employed as a starting material in preparing the reaction products of the present invention comprises the aliphatic thioethers in which only one of the radicals attached to the thioether sulfur atom contains an unsaturated linkage. Examples of this group are ethyl vinyl sulfide, ethyl isopropenyl sulfide, and the like.

While suitable reaction products of this invention may be prepared from the above types of unsaturated ethers, it is preferred that both radicals attached to the ether oxygen or thioether sulfur groups contain unsaturated (preferably olefinic) linkages, since the adduct formed therefrom usually contains a relatively large fraction having superior lubricating properties. The following are illustrative examples of such poly-unsaturated ethers: divinyl ether, diisopropenyl ether, diallyl ether, dicrotyl ether, dimethallyl ether, di(alpha-methyl-allyl) ether, (1-butene-3-yl) (2-butene-4-yl) ether, dihexenyl ether, allyl (2-methyl-4-pentene-2-yl) ether, allyl linalyl ether, etc., as well as the halogenated derivatives of the type of hexachlorodivinyl ether, etc. The corresponding thioethers in which each radical attached to the sulfur atom contains an unsaturated linkage between two carbon atoms include divinyl sulfide, di(beta-chlorovinyl) thioether, diallyl sulfide, dicrotyl sulfide, dimethyallyl sulfide, dihexenyl sulfide, and the like, and their homologs and analogs.

The ethers employed as the starting material for the preparation of the present lubricants may also contain more than one ether oxygen atom and/or thioether sulfur atom, this group of unsaturated ethers being represented by compounds of the type of 1,2-bis(vinyloxy) ethane, 1,3-bis-

(vinyloxy) propane, 1,2-bis(allyloxy) ethane, and the like, as well as by the unsaturated disulfides, such as divinyl disulfide.

At times, especially for extreme pressure purposes, it is highly desirable that halogen atoms be present in the final reaction product. For this purpose, in accordance with the present invention, the reaction products may be prepared from adducts involving a halogenated unsaturated organic compound. Such halogenated unsaturated compounds may contain one or more unsaturated linkages, preferably of olefinic character. These compounds may contain one or more halogen (i. e. chlorine, bromine, iodine, and/or fluorine) atoms which may be attached to saturated or unsaturated carbon atoms of the compound.

Examples of such halogenated hydrocarbons are: vinyl halides, allyl halides, 2-halo-propylene, crotyl halides, isocrotyl halides, 4-halo-1-butene, methallyl halides, 2-halo-2-butene, mono-halogenated-acetylenes, propargyl halides, 1,1-dihalo-ethylenes, 3-halo-1-pentene, 3-halo-cyclohexene, 2-halo-1,4-diphenyl-2-butene, 3-halo-1,4-pentadiene and their homologs. The above class of halogenated compounds may be further substituted in the nucleus and/or in the substituents in various degrees by straight-chain, branched chain, carbocyclic, and/or heterocyclic radicals, and by such substituents as alkoxy, alkenoxy, aryloxy, alkylimido groups and the like. Also, the organic compounds of the above class may contain two or more halogen atoms which may be attached to saturated and/or unsaturated carbon atoms.

As stated hereinbefore, the adducts from which the present reaction products are derived are formed by reaction of one or more of the above unsaturated organic compounds with hydrogen sulfide or a mercaptan or polymercaptan. Any sufficiently stable aliphatic mercaptan is suitable as a reactant for the formation of such adducts. A suitable aliphatic mercaptan may contain one or more sulfhydryl groups or radicals. In the majority of cases it is preferable to employ the normal or isoalkyl chain mercaptans of primary, secondary or tertiary character, particularly those containing in or derived from petroleum or petroleum products. The methyl, ethyl, butyl, amyl, hexyl, heptyl, octyl and the like mercaptans as well as their homologs, analogs, and substitution products, may be employed with excellent results.

Another group of mercaptans which may be employed as one of the two reactants comprises the dimercaptans, and particularly the polymethylene dimercaptans of the general formula $(HS(CH_2)_nSH$. This group of mercaptans may be reacted with, for example, aliphatic hydrocarbons containing a plurality of unsaturated linkages to produce polythioethers having a high molecular weight.

A particularly suitable group of unsaturated organic compounds which may be employed with these dimercaptans includes the unsaturated compounds containing unsaturated lingages of aliphatic character in alpha and omega positions (i. e. in terminal positions). Thus, by the "abnormal" type of addition, described hereinafter, the resulting products predominate in or consist of mercaptothioethers and polythioethers. Instead of employing aliphatic straight chain polyunsaturated hydrocarbons, it is also possible to use branched chain hydrocarbons or substituted derivatives thereof, provided such compounds contain at least one, and preferably two or more

unsaturated linkages of aliphatic character. These polyunsaturated organic compounds may or may not have unsaturated linkages in alpha and omega positions.

The formation of the subject adducts may follow two general courses, dependent upon the conditions (especially the catalyst) employed. First, the addition may take place according to the mechanism in which the sulfur atom of the hydrogen sulfide or mercaptan attaches predominately to the unsaturated carbon atom holding the greatest number of hydrogen substituents. Secondly, the mechanism may be that whereby the sulfur atom of the hydrogen sulfide or mercaptan attaches predominantly to the unsaturated carbon atom holding the fewer hydrogen substituents.

The first mechanism referred to above is termed "abnormal" addition, since it follows a course contrary to that postulated by Markownikoff's rule. The "abnormal" addition is promoted by the presence of such catalysts as ultra violet light, peroxides, oxygen, air, etc. This addition reaction occurs according to the "rule" advanced by Posner (Berichte 38, 646 [1904]).

The second mechanism referred to above is promoted by the presence of such catalysts as aluminum chloride, silicon tetrachloride, titanium tetrachloride or basic catalysts such as pyridine, piperidine, alkali metal hydroxides, alkaline earth metal hydroxides, and primary, secondary and tertiary amines.

The catalyst may be used in a wide range of concentrations, but preferably is present in amounts from about 1 mol percent to about 10 mol percent, based on the total mols of reactants present. Optimum results are obtained when the catalyst concentration is from about 2 to about 5 mol percent.

The ratio of unsaturate to hydrogen sulfide or mercaptan may vary within relatively wide limits, but preferably is between 0.5 and 2 mols unsaturate to 1 mol hydrogen sulfide or mercaptan.

The temperature at which the reaction is conducted will depend to a certain extent on the concentration, activity and stability of the catalyst. If temperatures above about 150° C. are used when the catalyst concentration is as high as 10 mol percent, the reaction may become violent, even to the point of explosion. However, if an active catalyst is present, even in amounts as low as about one mol percent, the reaction will proceed at a satisfactory rate at temperatures as low as about 40° C. It is preferable, from an economic and control standpoint, and when using about 2½ mol percent of a catalyst, to maintain the temperature within the range from about 75° C. to about 150° C.

The time for which the adduct reaction is allowed to proceed will vary with the activity of the catalyst and the temperatures being employed. Usually the reaction will be completed, when the other conditions are as stated hereinbefore, in from about 1 to about 48 hours, and close control of the reaction is obtained when conditions are such that the reaction time is from about 2 to 10 hours.

Diluents may or may not be used, as desired. While they are not essential, their use at times may be preferable in order to reduce the viscosity of the reaction mixture, to act as a mutual solvent for the reactants and catalyst, or to reduce the concentration of the reactants, thus allowing close control of the course of the reaction. Preferably, the diluent is substantially inert with respect to the reactants or catalysts. Saturated hydrocarbons are useful for this purpose. However, reactive diluents may be used for the purpose of initiating or terminating polymer chains, so as to give adducts having modified properties, as more particularly pointed out hereinafter.

The reaction proceeds at its optimum rate if retardants, such as hydroquinone, piperidine and certain metal salts, are absent. Upon completion of the formation of the adduct, the product is further treated to eliminate that fraction of the product which is too volatile, or otherwise unsuitable, for use as a lubricant. This treatment may vary with the product and the type of lubricant desired, but usually comprises selective solvent extraction for the removal of catalyst and undesirable fractions, or partial distillation, usually under diminished pressure, or a combination of these two steps.

An essential feature of the present invention is the substantially complete removal of the volatile components of the adduct. Since the adduct reaction usually results in the formation of a mixture of products, this relatively volatile fraction will vary, dependent upon the conditions under which the adduct is formed. Generally, the fraction volatilizing below about 100° C. at 0.2 cm. mercury pressure is preferably removed in order to obtain a lubricant having optimum properties.

The lubricant so obtained may be further treated in order to improve color, alter terminal groups, etc., if desired.

The various substances described above may be chain-like monomers or polymers containing one or more terminal hydroxyl groups. These hydroxyls may be acted upon by well known methods with such materials as etherifying or esterifying agents in order to obtain products having altered properties, such as solubility, or improved action as lubricants.

Various etherifying agents may be used for etherifying the terminal hydroxyls. These include alkyl halides, such as methyl iodide, methyl bromide, ethyl chloride, propyl iodide; aralkyl halides, such as benzyl chloride and methylbenzyl chloride; hydroxyalkyl chlorides, such as hydroxyethyl chloride; carboxyalkylating agents, such as sodium monochloracetate; and alkylene halides, such as allyl chloride. Ordinarily, the etherification is carried out in strongly basic environment, sodium hydroxide, liquid ammonia and quaternary ammonium bases and salts being the usual basic substances present.

Esterification of terminal hydroxyls may be accomplished with various inorganic groups such as nitrates, phosphates or sulfates. However, preferred esterifying agents are the organic acids, anhydrides or acid chlorides, and especially fatty acid anhydrides and their chlorides, including, for example, formic, acetic, propionic, butyric, hexoic, 2-ethylhexoic, acids and acid chlorides, and higher fatty acids such as lauric, stearic, myristic, palmitic and capric acids. Usually, the esters are formed by treatment of the hydroxylated adduct with the anhydride of the acid in the presence of a catalyst such as sulfuric or phosphoric acid. The saturated fatty acids form the most stable esters.

At times it is preferable to allow only partial etherification or esterification, thus forming half-ethers or half-esters instead of the di-ethers, or di-esters sometimes theoretically possible. For

other purposes end group hydroxyls may not only be partially or completely esterified or etherified, but also may be treated as to result in the formation of mixed ethers, mixed esters or ether-esters.

Etherification or esterification of the end-groups may take place simultaneously with or subsequent to adduct formation or may be effected prior to or subsequent to any decolorizing and purifying processes such as those described hereinbefore. Preferably, the end-group modification is carried out immediately after adduct formation and before purification or decolorizing.

When ethers or thioethers having unsaturated linkages in both radicals attached to the ether oxygen or thioether sulfur atom are treated with hydrogen sulfide or a mercaptan as described hereinbefore, the adducts are compounds having units of the general configuration:

$$—S—R—X—R—$$

wherein X is either sulfur or oxygen (dependent upon whether an ether or a thioether was used) and each R is an organic radical, preferably a saturated hydrocarbon radical.

When the adduct is formed from hydrogen sulfide and an oxyether having unsaturated linkages in both radicals attached to the ether oxygen atom, the polymer has the general formula:

$$R_1—[S—R_2—O—R_3]_m—R_4$$

wherein R_2 and R_3 represent like or different substituted or unsubstituted hydrocarbon radicals, m is an integer, R_1 represents the hydrogen atom or a radical such as $—CH=R_5—O—R_6—$, and R_4 represents the sulfhydryl radical or a radical such as $—S—R_7—O—R_8=CH_2$, wherein R_5 through R_8 represent like or different substituted or unsubstituted hydrocarbon radicals. An outstanding member of this group is the adduct of diallyl ether and hydrogen sulfide. When an unsaturated thioether is treated with hydrogen sulfide, the polymer corresponds to that above, except that the oxygen atoms are all replaced by sulfur atoms, thus giving a polymer having a high sulfur content, especially useful for extreme pressure lubrication. An outstanding member of this group is the adduct of diallyl sulfide and hydrogen sulfide.

To more clearly illustrate the present invention, the following examples are presented. It is to be understood, however, that various modifications can be resorted to without departing from the spirit of the invention as presented in the subjoined claims.

EXAMPLE I

Equal molar quantities of hydrogen sulfide and diallyl ether were introduced in the liquid state into a chilled quartz bomb tube which was sealed under a high vacuum. The tube was then warmed to about 0° C., disposed in a quartz container packed with ice, and subjected to illumination from a 400 watt quartz mercury arc lamp disposed at a distance of about 6 inches from the bomb. The irradiation was continued for about eighty minutes. During this period, the volume of the solution in the bomb decreased about 15%, most of this contraction occurring during the first 20 minutes of irradiation. The reaction product was a water-white liquid which was distilled to a temperature of about 235° C. under a pressure of about 2.3 cm. (mercury) to separate the relatively lighter boiling constituents which amounted to about 8% by weight of the total. The residue fraction remaining from the aforesaid distillation was found to have the following properties:

Molecular weight (cryo. benzene)	674
Sulfur, percent by weight	24.8
Mercaptan, as sulfur, percent by weight	5.1
Viscosity index	152
Viscosity at 100° F., in centistokes	66.6
Viscosity at 210° F., in centistokes	13.26
S. A. E	30
Micro pour point, °C	−45
Yield, percent by weight	92

From the above and other analyses it appears that this poly-addition product, on the average, has the following structural formula:

$$CH_2=CH—CH_2—O—(CH_2)_3—[S—(CH_2)_3—O—(CH_2)_3]_4—SH$$

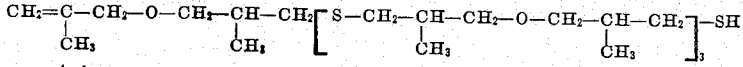
This product has a molecular weight of 660, a sulfur content of about 24% by weight, and a mercaptan content (as sulfur) of 4.85% by weight.

EXAMPLE II

Equimolar amounts of liquefied hydrogen sulfide and dimethallyl ether were introduced into a quartz bomb and irradiated with light emanating from a quartz mercury arc lamp under the same conditions as those employed in Example I. The reaction was continued for about 2 hours. The reaction product was then heated to 240° C. at a pressure of about 2 cm. (absolute). This caused the distillation of about 17% of the total product. An analysis of the remaining fraction gave the following results:

Molecular weight (cyro.-benzene)	661
Sulfur, wt. percent	23.1
Mercaptan, as sulfur, wt. percent	7.8
Micro pour point, °C	−35
Viscosity at 100° F., in centistokes	62.71
Viscosity at 210° F., in centistokes	10.01
Viscosity index	136
S. A. E	20
Yield, wt. percent	83

From the above, it appears that this methallyl ether-hydrogen sulfide addition product has the following average structure:



EXAMPLE III

The apparatus employed in this run consisted of a 500 cc. 3-neck flask equipped with a condenser, a quartz thimble holding a 100-watt mercury arc lamp projecting downwardly from the center neck to a point about 0.5 cm. above a sintered glass bubbler built into the bottom of the flask. Approximately 180 cc. of divinyl ether were introduced into the flask, which was maintained at a temperature of about 0° C. The contents of the flask were then illuminated with the above-mentioned lamp and approximately 0.28 mole of hydrogen sulfide were bubbled into the liquid divinyl ether at a rate of approximately 220 cc. per minute. About 15 minutes after the starting of the run a small amount of a white solid began to form on the walls of the flask. At the end of the run the reaction mixture was distilled. After removal of the unreacted divinyl ether approximately 30% of the remaining reaction mixture boiled above 240° C. at a pressure of about 1 cm. (absolute). This addition product had a viscosity index of 144.

EXAMPLE IV

Di-(beta-mercapto ethyl) ether and diallyl ether were reacted in substantially equimolar amounts, the interaction being effected photochemically under the deliberate influence of ultraviolet radiations emanating from a quartz mercury arc lamp. The reaction was continued for about one hour during which time the volume of the reactants in the quartz vessel decreased by about 15%. The reaction product was a water-white, viscous liquid. This product was subjected to distillation to produce a residual fraction boiling above 240° C. at a pressure of 8 mm. This residual fraction had the following properties:

Molecular weight	871
Pour point, °C	−39
Sulfur, per cent by wt	28.5
Mercaptan, as sulfur, per cent by wt	6.6
Viscosity index	151
S. A. E	20

From the above, it appears that this addition product has the following average structural formula:

$$HS-(RS)_5-RSH$$

wherein R represents $-(CH_2)_3-O-(CH_2)_3-$

EXAMPLE V

Equimolecular amounts of hydrogen sulfide and diallyl ether together with 5 mol percent ditertiary-butyl peroxide were heated in an autoclave at 100° C. for 30 hours. The fraction of the product boiling above 240° C., at 0.2 cm. mercury pressure (70% of the charge) had the following properties:

Viscosity, centistokes at 100° C	77.0
Viscosity, centistokes at 210° F	13.0
Viscosity index	143
S. A. E	30
Pour point, °F	−60

EXAMPLE VI

One hundred sixteen parts allyl alcohol, 35 parts hydrogen sulfide and 12.9 parts di-normal-butylamine were heated together in an autoclave at 100° C. for 48.5 hours. The product was subjected to distillation, the lubricating fraction being that part of the product boiling above about 134° C. at 0.3 cm. mercury pressure, and consisting essentially of bis(beta-hydroxy-alpha-methylethyl) sulfide. A by-product obtained in the condensation was beta-hydroxy-alpha-methylethyl mercaptan.

The above reaction products may be dispersed in water or any other aqueous medium in minor amounts in order to obtain excellent cutting and metal working lubricants. Generally, the amount of adduct added need not exceed 5% by weight and amounts of from 1 to 5% have been found to be desirable. However, higher concentrations may be used and under some conditions above 10% and higher may be used.

To further improve metal working lubricants of this invention minor amounts generally of less than 1% by weight and preferably between about 1.15 and 0.5% of a corrosion inhibitor may be added to the aqueous emulsion. The corrosion inhibitors suitable for use in compositions of this invention may be any soluble inhibitor which does not interfere with the function of

the extreme pressure reaction product of this invention or have any other deleterious effect either on the composition, the metal being machined, or on the user of the composition. Among the corrosion inhibitors which may be used are organic and inorganic nitrites, alkali borates, chromates, dichromates, silicates, phosphates, carbonates, soaps, such as chromium soaps, alkanolamine soaps, alkali metallic soaps of water-soluble sulfonic acids, and the like. Particularly preferred corrosion inhibitors are the nitrite salts of organic nitrogen bases. The organic bases preferably used in preparing these inhibitors include primary, secondary and tertiary amines and quaternary ammonium bases.

Specific examples of suitable organic nitrogen bases are listed below:

Primary amines.—Methylamine, 2-amino-3-methylbutane, isopropylamine, isobutylamine, various hexyl, heptyl, octyl, nonyl, decyl, dodecylamines; paraffin wax amines prepared by chlorination of paraffin wax and ammonolysis of the product; cyclohexylamine, trimethyl cyclohexylamine, benzylamine, beta phenyl ethyl amines, tetrahydrobetanaphthylamine, allylamine, etc.

Secondary amines.—Methyl n-butylamine, methyl isobutylamine, methyl tertiary butylamine, methyl amylamine, amylhexylamine, n-methyl cyclohexyl amine, dicyclohexylamine, methyl benzylamine; corresponding ethyl, propyl and higher amines; dibenzylamine, di(beta phenyl ethyl) amine; piperidine, piperazine, morpholine, etc.

Tertiary amines.—Tri-ethylamine, tri-n-propylamine, tri-isopropylamine, tri-butylamine, triamylamine, higher trialkylamines, having, if desired, different alkyl radicals, including alicyclic and alkaryl radicals such as dimethyl benzyl amine, methyl dibenzylamine, dimethyl cyclohexylamine, methyl cyclopentamethyleneamine, etc.

Quaternary ammonium bases.—Trimethyl hexylammonium, corresponding cyclohexyl, heptyl, ethyl cyclohexyl, benzyl, octyl, nonyl, trimethyl cyclohexyl, decyl, dodecyl, hexadecyl, octadecyl, paraffin wax, etc., ammonium bases, tri-ethyl, tri-propyl, tri-butyl, etc. ammonium bases corresponding to the above; alkyl pyridinium and similar bases as butyl, amyl, hexyl, cyclohexyl, heptyl, methyl cyclohexyl, benzyl, etc.; pyridinium or quinolinium bases, etc.

These corrosion inhibiting salts should have a sufficient number of carbon atoms to impart necessary solubility and as a rule the nitrogen base should have at least 5 carbon atoms although bases having less than 5 carbon atoms may be utilized. Also the hydrocarbon radicals may contain attached thereto polar radicals such as chlorine, ether, sulfide, alcohol, amine, etc. radicals.

A few of the compounds which are particularly preferred from this class are benzyltrimethylammonium nitrite, morpholic nitrite, dibenzylamine nitrite, 3,3,5-trimethylcyclohexylamine nitrite, cyclohexylamine nitrite, dicyclohexyl amine nitrite, beta-phenylethylamine nitrite, 2,4,4,6-tetramethyl tetrahydro 1,3-oxazine nitrite, methyl isobutyl carbamine nitrite, piperidine nitrite, dicyclohexylammonium nitrite, dicycloisopropylammonium nitrite, etc.

If desired a minor amount of masking or perfuming agent may be added to improve the odor of the composition. Among such materials may be included low molecular weight aldehydes,

e. g. acetaldehyde, copper sulfate, oil of pines, oil of mirbane and the like. Or the odor of the reaction product may be improved by mild oxidation or acetylation with acid halides, ketene, etc.

Reaction products may be used with any desirable cutting oil emulsion particularly under extreme pressure conditions. In cases where an emulsion is used, the diallyl ether-H_2S adduct is added to the aqueous phase and the entire emulsion stabilized with a coupling or detergent agent. Any coupling agent may be used among which are the soluble salts of petroleum sulfonic acids such as sodium petroleum sulfonate; alkali soaps of fatty acids, rosin acids, petroleum acids; alkali salts of sulfated alcohols, e. g. sodium oleyl sulfate, sodium lauryl sulfate, sodium ocenol sulfate; alkali salts of mono and polyalkyl esters of sulfo-dicarboxylic acid, etc.

Effective metal working lubricants in accordance with the present invention may be made after the following formulation:

	Broad Range, Per Cent Weight	Preferred Range
Water or aqueous base	75–99	85–95
Reaction product of the invention, i. e. diallyl ether-H_2S adduct	1–25	2–10
Corrosion inhibitor, e. g. dicyclohexylammonium nitrite	0–2	0.05–0.5
Perfuming agent	0.1	0.1–0.5

Evaluation of composition of this invention may best be illustrated by the four-ball extreme pressure lubrication tester similar in principle to the Boerlage apparatus described in the magazine Engineering, vol. 136, July 14, 1933. 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 composition to be tested. Tests were run under conditions indicated in the table and compared with other outstanding cutting composition to be tested. The diameter of the wear scars worn on the three balls forming the base of the pyramid were measured, and the average taken as the true indication of wear.

angle, cutting, speed, general cutting conditions, e. g. tool rigidity and the like.

	Composition	Minimum Critical Rake Angle
1	Dry Cutting	26–27
2	Straight Mineral Oil	21
3	Sulfurized Mineral Oil	16
4	5% bis (γ-hydroxy propyl) disulfide in 95% water	11

The importance of maintaining the rake angle of a tool at a minimum is that such tools are much stronger thereby resulting in increased tool life, the coefficient of friction between tool and chip is much lower and worked piece surface is much smoother and of better appearance.

It has also been observed that keeping the critical rake angle constant, the force on the tool using compositions of this invention is at least half of that required when cutting dry and at least 30% less than that required when using the best known cutting emulsion containing sulfurized materials and other extreme pressure agents.

Aqueous composition of this invention may be easily inhibited against corrosion for long periods of use by addition of a minor amount, generally less than 1% of an inhibitor as referred to previously. Thus the following test was performed in which metal strips were immersed in compositions as denoted in the table and observed for signs of corrosion.

	Composition	Corrosion Time (Days)
1	5% bis (γhydroxy propyl) disulfide in 95% water	1 day.
2	5% bis (γhydroxy propyl) disulfide in 95% water plus 0.05% dicyclohexylammonium nitrite.	3 days.
3	5% bis (γhydroxy propyl) disulfide in 95% water plus 0.05% diisopropylammonium nitrite.	3 days.

The present compositions may be applied with excellent results to general cutting operations where cooling and lubricating of the tool and work piece under adverse conditions is encountered. The present invention having thus been fully described is not to be limited by any specific examples which have been presented herein solely for the purpose of illustration, but only by the following claims.

Effects of various materials on extreme pressure lubrication characteristics of soluble oil emulsions

[4-ball extreme pressure lubrication tester, 1500 R. P. M., steel against steel.]

	Lubricant	40	60	80	100	120	140	150	200	300
1	30% Base X in water [1]	.40	.48	1.93	2.52	------	Welded	------	------	--------
2	15% Base X in water	.35	.43	2.12	2.93	------	Welded	------	------	--------
3	3% tricresyl phosphate in 15% Base X Emulsion	.35	.46	2.04	2.24	------	Welded	------	------	--------
4	5% bis(γ-hydroxy-propyl) disulfide in 15% Emulsion of Base X	.38	.43	.49	.54	.55	.60	------	------	--------
5	5% bis (γ-hydroxy-propyl) disulfide in 4% rosin soap emulsion	------	.47	.52	.62	------	----------	------	1.16	Welded

[1] Base X consists of: 70.5% 200 neutral mineral oil; 27.5% Na petroleum sulfonate; 2.0% water; 0.5% o-phenyl phenol.

Another method of evaluating improvement of cutting compositions is by measuring the minimum critical rake angle of the cutting tool at which it is still possible to obtain a smooth machining surface. This critical rake angle may be defined as the rake angle of the tool at which the transformation from a rough to smooth surface occurs under cutting conditions other things being constant, such as depth of cut, clearance

We claim as our invention:

1. A cooling and lubricating composition comprising a major amount of water, a minor amount, sufficient to impart extreme pressure properties to the composition of a bis(gamma-hydroxy propyl) sulfide, and a corrosion inhibiting amount of dicyclohexylammonium nitrite.

2. A cooling and lubricating composition comprising a major amount of an aqueous medium, a minor amount, sufficient to impart extreme pressure properties to the composition of a bis(gamma-hydroxy propyl) sulfide, and a corrosion inhibiting amount of di-isopropylammonium nitrite.

3. A cooling and lubricating composition comprising a major amount of an aqueous medium, a minor amount, sufficient to impart extreme pressure properties to the composition of a bis(gamma-hydroxy propyl) sulfide and a corrosion inhibiting amount of a nitrite salt of an organic nitrogen base.

4. A cooling and lubricating composition comprising a major amount of an aqueous medium, a minor amount, sufficient to impart extreme pressure properties to the composition of a bis(hydroxy alkyl) sulfide and a corrosion inhibiting amount of a nitrite salt of an organic nitrogen base.

5. A soluble lubricating composition comprising a major amount of an aqueous medium and a minor amount, sufficient to impart extreme pressure properties to the lubricant of a bis(gamma-hydroxypropyl) sulfide having a boiling point above 160° C. at 0.2 cm. mercury pressure.

6. A soluble lubricating composition comprising a major amount of an aqueous medium and a minor amount, sufficient to impart extreme pressure properties to the lubricant of a bis(hydroxyalkyl) sulfide having a boiling point above about 160° C. at 0.2 cm. mercury pressure.

7. A cooling and lubricating composition comprising a major amount of water and a minor amount sufficient to impart extreme pressure properties to the composition, of a polymeric adduct of an aliphatic organic compound having at least one unsaturated linkage between two carbon atoms and being selected from the class consisting of unsaturated aliphatic ethers and unsaturated aliphatic alcohols, the separate unsaturated aliphatic radicals thereof having not more than four carbon atoms and hydrogen sulfide obtained by reacting said materials in the mol ratio of 0.5–2 to 1 mol, respectively, at a temperature ranging from about 75 to 150° C. for a period of from about 2 to 10 hours and thereafter removing volatile components of said polymeric adduct so that said adduct has a boiling point substantially above about 160° C. at 0.2 cm. mercury pressure.

8. A cooling and lubricating composition comprising a major amount of water and a minor amount sufficient to impart extreme pressure properties to the composition, of a polymeric adduct of an aliphatic unsaturated aliphatic ether having not more than four carbon atoms in each of the aliphatic radicals thereof and hydrogen sulfide obtained by reacting said materials in the mol ratio of 0.5–2 to 1 mol, respectively, at a temperature ranging from about 75 to 150° C. for a period of from about 2 to 10 hours and thereafter removing volatile components of said polymeric adduct so that said adduct has a boiling point substantially above about 160° C. at 0.2 cm. mercury pressure.

9. A cooling and lubricating composition comprising a major amount of water and having incorporated therein a minor amount, sufficient to impart extreme pressure properties to the composition of a polymeric adduct of an unsaturated aliphatic alcohol having not more than four carbon atoms in the aliphatic radical and hydrogen sulfide obtained by reacting said materials in the mol ratio of 0.5–2 to 1 mol, respectively, at a temperature ranging from about 75 to 150° C. for a period of from about 2 to 10 hours and thereafter removing volatile components of said polymeric adduct so that said adduct has a boiling point substantially above about 160° C. at 0.2 cm. mercury pressure.

10. A cooling and lubricating composition comprising a major amount of water and having incorporated therein a minor amount, sufficient to impart extreme pressure properties to the composition of a polymeric adduct of an aliphatic organic compound having at least one unsaturated linkage between two carbon atoms and being selected from the class consisting of unsaturated aliphatic ethers and unsaturated aliphatic alcohols, the separate unsaturated aliphatic radicals thereof having not more than four carbon atoms and hydrogen sulfide obtained by reacting said materials in the mol ratio of 0.5–2 to 1 mol, respectively, at a temperature ranging from about 75 to 150° C. for a period of from about 2 to 10 hours and thereafter removing volatile components of said polymeric adduct so that said adduct has a boiling point substantially above about 160° C. at 0.2 cm. mercury pressure and about 1% of a nitrite salt of an organic nitrogen base.

11. A cooling and lubricating composition comprising a major amount of water and a minor amount sufficient to impart extreme pressure properties to the composition, of a polymeric adduct of an aliphatic unsaturated aliphatic ether having not more than four carbon atoms in each of the aliphatic radicals thereof and hydrogen sulfide obtained by reacting said materials in the mol ratio of 0.5–2 to 1 mol, respectively, at a temperature ranging from about 75 to 150° C. for a period of from about 2 to 10 hours and thereafter removing volatile components of said polymeric adduct so that said adduct has a boiling point substantially above about 160° C. at 0.2 cm. mercury pressure and a corrosion inhibiting amount of a nitrite salt of an organic nitrogen base.

12. A cooling and lubricating composition comprising a major amount of water and a minor amount, sufficient to impart extreme pressure properties to the composition, of an adduct of a dialkenyl ether having not more than four carbon atoms in each of the alkenyl radicals and hydrogen sulfide obtained by reacting said materials in the mol ratio of 0.5–2 to 1 mols respectively, at a temperature ranging from about 75 to 150° C. and for a period of from about 2 to 10 hours and thereafter removing volatile components of said adduct so that said adduct has a boiling point substantially above about 160° C. at 0.2 cm. mercury pressure.

13. A cooling and lubricating composition comprising (*a*) about 5% of bis(hydroxyalkyl) sulfide in (*b*) about 15% emulsion base consisting of 70.5% mineral oil, 27.5% Na petroleum sulfonate, 2% water and 0.5% o-phenyl phenol, said composition being dispersed in (*c*) about 80% water, all percentages being based on total composition.

14. A cooling and lubricating composition comprising (*a*) about 5% bis(hydroxyalkyl) sulfide and (*b*) about 4% rosin soap emulsion, said composition being dispersed in (*c*) 91% water, all percentages being based on total composition.

15. A cooling and lubricating composition comprising (*a*) about 5% of bis(α-hydroxypropyl) sulfide in (*b*) about 15% emulsion base consisting of 70.5% mineral oil, 27.5% Na petroleum sul-

fonate, 2% water and 0.5% o-phenyl phenol, said composition being dispersed in (c) about 80% water, all percentages being based on total composition.

16. A cooling and lubricating composition comprising (a) about 5% bis(α-hydroxypropyl) sulfide and (b) about 4% rosin soap emulsion, said composition being dispersed in (c) 91% water, all percentages being based on total composition.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,562,844 July 31, 1951

DENHAM HARMAN ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 13, lines 22 and 28, after "soluble" insert *cooling and*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 22nd day of January, A. D. 1952.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.