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3,798,164

POLYOXYALKYLENE BIS-THIOUREA EXTREME PRESSURE AGENTS AND METHODS OF USE

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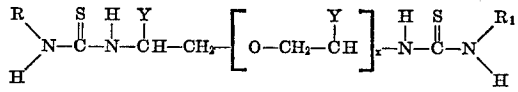
No Drawing. Original application May 24, 1971, Ser. No. 146,535, now Patent No. 3,704,321. Divided and this application Sept. 14, 1972, Ser. No. 289,203

Int. Cl. C10m *1/06, 1/38*

U.S. Cl. 252—47.5 6 Claims

ABSTRACT OF THE DISCLOSURE

Novel substituted and unsubstituted polyoxyalkylene bis-thioureas having the formula:



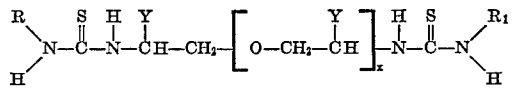
wherein x is a number from 1 to 10, R and R_1 are selected from the group consisting of hydrogen, alkyl and alkenyl, Y is hydrogen or lower alkyl, are useful as extreme pressure lubricants in metal working fluids and particularly in aqueous type fluids. Compositions comprising the thioureas and a boundary lubricant provide the anti-weld and friction reduction properties necessary for heavy duty machining.

This is a division of application Ser. No. 146,535, filed May 24, 1971, now U.S. Pat. 3,704,321, dated Nov. 28, 1972.

BACKGROUND OF THE INVENTION

This invention relates to a series of new and useful bis-thiourea compounds including compositions and methods of using the same in machining operations. More specifically, it has been discovered that certain novel polyoxyalkylene bis-thioureas and their compositions perform as extreme pressure agents when incorporated into metal working fluids. The invention is founded on the realization that superior extreme pressure lubrication can be expected in heavy duty machining operations particularly with aqueous base cutting fluids when used in conjunction with the thioureas defined herein below. The instant thioureas are significant in that there are few sulfur containing extreme pressure agents available which can be effectively employed in a wide range of aqueous systems. Thus, the instant compounds permit water-based metal working solutions and emulsions to be used in a broader range of machining applications including heavy duty grinding and cutting operations.

Briefly, it has been discovered that a series of thioureas having the formula:



wherein x is a number from 1 to 10 and R and R_1 are selected from the group consisting of hydrogen, alkyl and alkenyl and Y is hydrogen or lower alkyl, perform as extreme pressure (EP) agents in metal working fluids and particularly those containing water.

Along with the extreme pressure agents shown herein, it is often desirable though not required in each instance to also employ boundary lubricants. Boundary lubrication is ordinarily used in machining operations to prevent heat build-up and unwanted wear which liquids such as water, hydrocarbon oils, silicones etc. are unable to control especially as conditions become more extreme. However, it has been found that polar type boundary lubricants perform particularly well with the above mentioned thioureas. It is believed that these lubricants act with the extreme pressure agents to more effectively release sulfur from the thioureas to form protective iron sulfide films on the surface of the workpiece when subjected to conditions of high pressure and temperature. Therefore, in addition to novel polyoxyalkylene bis-thioureas, the present invention also contemplates compositions of said thioureas advantageously used with boundary lubricants sometimes referred to as lubricity agents to enhance the activity of the extreme pressure component.

As previously indicated, the EP additives of the present invention provide the necessary friction modification and wear reduction as well as galling and seizing reducing properties making them highy versatile and satisfactory extreme pressure lubricants, especially useful in aqueous metal working fluids. Heretofore, compositions used in heavy-duty machining operations were mostly limited to non-aqueous or oil-based fluids. Aqueous metal working fluids, on the other hand, ordinarily in the form of solution or emulsion comprised of water or diluted with water prior to use and perhaps containing in addition a boundary lubricant additive such as fatty acid soaps including sulfoesters, alkyl taurines, alkylpolyamines, polyethylene glycols, petroleum sulfonate, sulfoaminoacetates, have been limited to machining operations where only relatively light or mild pressure between the work and cutting tool would be employed.

Generally, water based metal working fluids used under light pressure provide sufficient lubrication to prevent metal-to-metal contact. However, as pressures and temperatures rise between work and tool to more extreme conditions, water-based compositions are unable to supply sufficient friction reduction or boundary lubrication. Frequently, pressure between the sliding chip and tool face is in the order of 100,000 p.s.i. with temperatures in the area of contact at 1000° F. or more. Under these conditions, aqueous films with boundary lubricants commonly break down, greatly diminishing tool life and quality of finish on the work.

Sulfur containing metal working lubricants and extreme pressure agents such as sulfurized mineral and fatty oils, sulfochlorinated oils and the like, have been used with some success. However, such products have not been entirely satisfactory in many instances. Frequently, extreme pressure soluble oils made with conventional sulfurized fatty additives have been undependable because of their instability. Blends of conventional sulfur containing extreme pressure additives and mineral oils either will not emulsify or will form inferior emulsions that "break" when stored or used. Then too, the more stable sulfurized products would not perform well because they did not release their sulfur under conditions of high temperature and pressure to provide essential EP lubrication.

Accordingly, it is a principal object of this invention to provide a series of novel polyoxyalkylene bis-thiourea extreme pressure agents and process for their manufacture.

Another principal object is to provide metal-working compositions comprising the bis-thiourea EP agents which possess good stability and shelf-life, but nevertheless release their sulfur to form protective films under conditions of high temperature and pressure.

Another object is to provide complete aqueous base metal working compositions for use under extreme conditions during heavy duty machining operations.

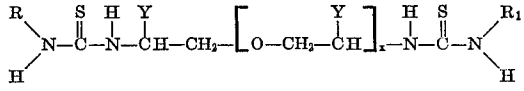
A still further object of the present invention is to provide a method of machining under conditions of extreme pressure and temperature with polyoxyalkylene bis-thiourea EP agents.

These and other objects, features and advantages of this invention will become apparent to those skilled in the

art after a reading of the following more detailed description.

SUMMARY OF THE INVENTION

As stated above, this invention relates to novel and useful thioureas. In particular, it is concerned with thioureas having their terminal nitrogens substituted and unsubstituted which can be represented by the following formula:



wherein x, R, R_1 and Y are as defined above. Their molecular weights are generally under 1000 and in most instances will range from about 250 to 950. Each of the R's may be hydrogen, but are preferably substituted with alkyl or alkenyl. When alkyl or alkenyl, they are advantageously 1 to 8 carbon atoms, which includes lower alkyl radicals of 1 to 3 or 4 carbon atoms such as methyl, ethyl and propyl as well as lower alkenyls like ethylene, propenyl and allyl. These groups also include higher alkyls and alkenyls usually up to 8 carbon atoms, however, lower members are preferred for better water solubility. The above formula contemplates in addition to normal aliphatic radicals their usual isomeric forms such as iso-propyl, butyl, secondary and tertiary butyl and the like. Y may be hydrogen, however, here too in most instances it will be lower alkyl of 1 to 3 carbon atoms like methyl, ethyl and propyl.

In the above formula, x is a number from 1 to 10 with an intermediate preferred range from about 3 to 6. Thioureas in which x is about 3 and 5.6 have been specially advantageous.

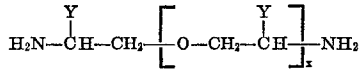
Specific examples of a few of the thioureas contemplated within the instant invention are represented in the following table.

TABLE I

R	R_1	Y	x
H—	H—	H—	2
H—	H—	CH_3—	6
CH_3—	CH_3—	CH_3—	2.6
C_2H_5—	C_2H_5—	CH_3—	6
CH_3—	CH_3—	CH_3—	5.6
C_3H_7—	C_3H_7—	CH_3—	5
C_2H_3—	C_2H_3—	CH_3—	6
C_7H_{15}—	C_7H_{15}—	C_2H_5—	4
C_2H_5—	C_2H_5—	H	6
C_2H_3—	C_2H_3—	H	5.6
C_4H_7—	C_4H_7—	H	3
C_6H_{11}—	C_6H_{11}—	H	9

Generally, the process for their preparation involves reacting a polyether diamine with an isothiocyanate. The reaction mixture is heated for several hours forming a homogeneous solution. The mixture is then treated to remove the solvent used to dissolve the reactants.

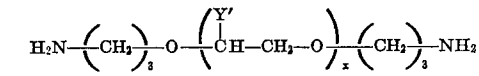
Broadly, the polyether diamine reactant of this invention is a polyoxyalkylene diamine. It encompasses both linear and branched members having at least one and preferably a plurality of ether linkages and containing two terminal primary amino groups. Their molecular weights generally range from about 100 to 700. These polyethers are substantially free from functional groups other than amino. They may have the following formula:



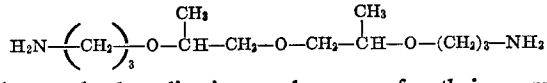
wherein Y is hydrogen or lower alkyl of 1 to 3 carbon atoms and x is a number from 1 to 10 and preferably about 3 to 6.

Illustrative of the polyoxyalkylene diamines which are appropriate in preparing products of the instant invention are polyoxyethylenediamine, polyoxypropylenediamine, polyoxybutylenediamine, polyoxyamylenediamine and polyoxyhexylenediamine. These polyethers are known, available products of commerce and are fully disclosed in U.S. Pats. 3,299,169 and 3,309,182 which are incorporated-by-reference herein. Polyethers of the kind described above are available under the trademark "Jeffamine" by Jefferson Chemical.

Alternatively, similar other amines of the following structure can be used:

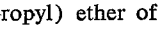


wherein Y' is hydrogen or lower alkyl of 1 to 3 carbon atoms and x is a number from 1 to 10. A preferred illustrative example of such glycol diamines is di-(3-aminopropyl) ether of dipropylene glycol having the formula:



These polyether diamines and process for their manufacture are taught in U.S. Pat. 3,316,185 which disclosure is incorporated-by-reference herein.

Isothiocyanates are reacted with the polyether diamines to form the adduct. Those isothiocyanates for use in the propyl) ether of dipropylene glycol having the formula:



wherein Z is hydrogen, alkyl or alkenyl. When Z is alkyl or alkenyl, they are radicals of 1 to 8 carbon atoms corresponding with the aforementioned R substituents. Illustrative examples of specific isothiocyanates are isothiocyanic acid and their corresponding esters such as methyl, ethyl, propyl, allyl, isopropyl and the like.

Before charging the reaction vessel, the reactants are separately dissolved in virtually any appropriate organic solvent such as benzene, acetone, toluene, xylene, various ethers like diethyl, methyl ethyl ethers as well as various alcohols such as methyl, ethyl, isopropyl, etc. The polyether amine reactant is preferably cooled below ambient temperature to compensate for the exotherm produced from mixing the reactants. Here, specific cooling temperatures are not critical but remain a factor based upon the rate at which the isothiocyanate and polyether are added together. Accordingly, the reactants should be slowly incorporated to avoid excessive heat build-up from the exothermic reaction. In most cases, the mole ratio for the reactants is about 2 moles of the isothiocyanate for each mole of the polyether diamine.

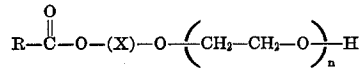
The reaction mixture is then heated, preferably under reflux conditions which are at temperatures in the range from 65 to 95° C. and more specifically at about 80° C. Heating should be continuous for several hours until a homogeneous solution forms which in most instances is water white to straw yellow in color. Solvents initially used to dissolve the reactants are then removed. This can be accomplished by several means, but most conveniently by stripping the mixture at reduced temperatures and pressures. The temperature is lowered to about 40 to 80° C. and the pressure reduced to 30 to 50 mm. Hg. Ordinarily, a solvent free product can be secured in about 1½ to 3 hours. The final polyoxyalkylene bis-thiourea is a glassy clear to light yellow liquid.

The polyoxyalkylene bis-thiourea extreme pressure lubricants of the present invention act by forming protective metal sulfides on the surface of the workpiece under extreme temperatures and pressures. However, optimal results can best be achieved if these EP agents are used in conjunction with boundary lubricants and specially polar type boundary lubricants. In the case of the latter, their polar ends, which may be the fatty acid or ester portion of the molecule, are absorbed onto the metal surface forming a film, and the non-polar portions provide added strength to the film through cohesion.

Preferred boundary lubricants include long chained aliphatic acid soaps having 8 to 22 carbon atoms in their acid moiety. The cationic moiety may be an alkali metal such as sodium potassium, lithium and ammonium. Others include morpholine, mono, di- and tri-ethanolamines,

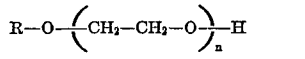
analogous isopropanolamines and mixtures thereof. Illustrative of this group are sodium stearate, ammonium laurate and triethanolamine-2-ethyl hexanoate. Other boundary lubricants are olefinic acid soaps having 8 to 22 carbon atoms in its straight or branched acid moiety along with 1 or more double bonds. The cationic portion may correspond to the foregoing aliphatic acid soaps. Members of this group include potassium abietate, diethanolamine linoleate and morpholine oleate.

A third group of boundary lubricants for use in the compositions disclosed herein are ethoxylated fatty acid esters of polyols of the formula:



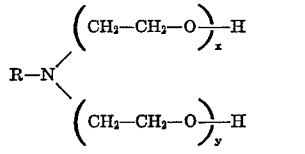
wherein R is a saturated, unsaturated, branched or unbranched chain having 7 to 21 carbon atoms, X corresponds to R, however, the former have chains of 2 to 16 carbon atoms containing one or more hydroxyl groups and *n* is 1 to 20. Included in this group are products available under the trademark "Ethofat" by Armour.

Other boundary lubricants for use in accordance with the instant invention are ethoxylated aliphatic or olefinic alcohols of the formula:



wherein *x* and *y* are numbers from 1 to 20. R represents 30 carbon atoms and *n* is 1 to 20. This group includes ethoxylated cetyl, stearyl or oleyl alcohols having 10 moles of ethylene oxide. Others are the polyoxyethylene substituted N,N' fatty acid amides available under the trademark "Ethomid" by Armour.

Additional agents useful in the instant compositions are ethoxylated amines of the formula:



wherein *x* and *y* are numbers from 1 to 20. R represents salts and aliphatic or olefinic acids of these amines having 8 to 22 carbon atoms such as oleic and stearic acid. They are sold by Armour under the trademark "Ethomeen." Specific preferred products are the C/15, C/20 and C/25 formulations. Further related products include ethoxylated diamines, salts and acids thereof which can also be employed with the thiourea EP agents. They include the "Ethoduomeen" line by Armour.

The present invention also contemplates compositions containing lower alkyl and natural esters of C_8 to C_{22} fatty acids such as methyl lardate, ethyl linoleate and methyl tallate.

Generally, EP lubricants of the present invention are used in an amount sufficient to provide anti-weld properties. Though not required in each instance, it is advantageous to employ in complete compositions the aforementioned boundary lubricants in an amount sufficient to enhance or activate the performance of the EP agent. The ratio of EP agent to boundary lubricant is used in the range from about 1:1 to 1:30. The combined concentration of EP agent and boundary lubricant in formulations should be from 2% to 85%, and when diluted for use, should have a concentration ranging from about 0.03% to 5% and preferably about 0.1% to 3.0%.

The extreme pressure agents of this invention can be formulated into numerous metal working compositions by incorporating the ingredients together using conventional, known techniques. The compositions will ordinarily be in the form of solutions and emulsions.

Complete metal working compositions are those containing usual base cutting fluids, and preferably for purposes of the instant invention aqueous base metal-working fluids. Aqueous type fluids are those containing water or are diluted with water prior to use. Aqueous base fluids may be of the soluble oil type which are water emulsifiable, and contain mineral oils as well as emulsifiers. Emulsifiers commonly used therewith may be the mahogany soaps, conventional soaps, rosin acid and tall oil soaps. Any number of nonionic and anionic surfactants such as sodium lauryl sulfate, including the phenolate, carboxylate, sulfonate surfactants and the like can be used with soluble oils.

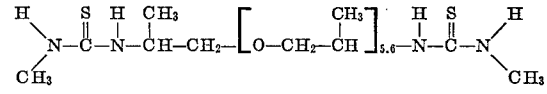
Compositions of this invention may also contain other adjuvants frequently used in metal working fluids such as coupling agents, anti-foam agents, corrosion inhibitors, bactericides, wetting agents, etc. Typical coupling agents are the glycol ethers available under the trademark "Cellosolve" which includes their methyl, ethyl and butyl homologues. Other such agents include butyl and amyl alcohol, various polyols and mixtures thereof.

Corrosion and rust inhibitors such as borax, sodium nitrite, alkanolamines like di- and tri-ethanolamines and condensation products of diethanolamine with fatty acids are frequently used. Anti-foam agents include conventional agents such as ester waxes, fatty acid esters of higher alcohols such as methyl stearate and tricresyl phosphate. Agents like O-phenol phenoxide, methyl p-hydroxy benzoate and quaternary amines such as "Dowicil 100" act to stabilize fluids against fungal or bacterial growth. The specific combination of additives used and their proportional range or ratio in each case will naturally vary depending on the kind of machining undertaken, the type of metal and operation, whether it is light, medium or heavy duty cutting, grinding, milling, broaching, or whatever.

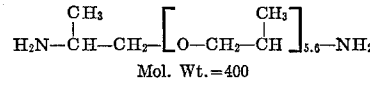
The polyoxyalkylene bis-thioureas can be used in a broad range of heavy-duty machining processes. Machining for purposes of this invention relates to all types of cutting and grinding on a general basis. There are no special limitations in their use, but can be employed whenever special lubrication is indicated. The workpiece is contacted with the fluid by any conventional method. Ordinarily, in the case of small bench and lathe work, manual methods can be used such as brush, roller or hand squirt can applicators. However, for larger floorstand production machines, pump pressure circulation, bath or jet spray methods will ordinarily be employed.

The following examples illustrate some of the embodiments of this invention. It is to be understood that these are for illustrative purposes only and do not purport to be wholly definitive as to conditions and scope.

EXAMPLE I



A 500 ml. four-neck round bottom flask fitted with a stirrer, thermometer, condenser and addition funnel was charged with 52.1 grams of a polyether diamine having the following formula:

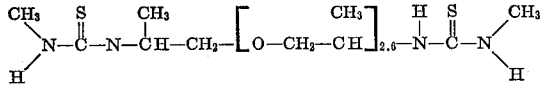


Mol. Wt.=400

and dissolved in 120 ml. of isopropyl alcohol. In a second flask, 37 grams of methyl isothiocyanate was dissolved in 75 ml. of isopropyl alcohol. The dissolved methyl isothiocyanate was slowly added to the dissolved polyether over a 45 minute period with stirring. During this time, a slight exotherm occurred. After the addition was completed, the reaction mixture was refluxed at the boiling point of the isopropyl alcohol and allowed to stand overnight. On the following day, the solvent was removed by means of a rotating vacuum evaporator. Evaporation was performed

at 60–70° C. and at approximately 30 mm. Hg pressure. The final product had the appearance of a clear oil.

EXAMPLE II



The above product was prepared according to the method of Example I, however, the polyether diamine starting material had a molecular weight of 230 and x was 2.6.

EXAMPLE III

	Wt. percent
EP agent of Example I	4.00
Methyl lardate	7.50
Paraffin oil	64.00
Butyl Cellosolve	2.00
Sodium petroleum sulfonate	22.00
Methyl p-hydroxybenzoate	0.50
	100.00

A kettle was charged with the EP agent, butyl Cellosolve, methyl lardate, methyl p-hydroxybenzoate and sodium petroleum sulfonate. The ingredients were warmed to 120 to 140° F. and blended until uniform at which time the paraffin oil was finally added with stirring.

EXAMPLE IV

	Wt. percent
EP agent of Example I	1.00
Butyl Cellosolve	1.00
Ethofat 242/25	6.00
Triethanolamine	10.00
Bactericide (Dowicil 100)	0.50
Water	81.50
	100.00

All ingredients were charged to an open kettle except the water. The composition was stirred until uniform. The water was then added to the kettle.

EXAMPLE V

Complete metal working composition

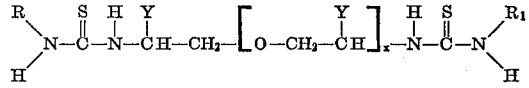
	Wt. percent
EP agent of Example II	6.00
Methyl lardate	2.00
Mineral oil	68.00
Water	1.20
Butyl Cellosolve	3.80
Dowicil 100 (Biocide)	0.70
Petroleum sulfonate; sodium salt	18.30
	100.00

The mineral oil and petroleum sulfonate salt were added to an open head kettle. The EP agent and methyl lardate were then blended into the mineral oil-sodium petroleum sulfonate solution. Finally, the Dowicil 100-water-butyl Cellosolve was added as a pre-blend. The blending was carried out at a temperature in the range of 100° to 140° F.

While the invention has been described in conjunction with specific examples thereof, this is illustrative only. Accordingly, many alternatives, modification and variations will be apparent to those skilled in the art in light of the foregoing description, and it is therefore intended to embrace all such alternatives, modifications and variations as to fall within the spirit and broad scope of the appended claims.

We claim:

1. A method of machining a metallic workpiece under conditions of high temperature and pressure, which method comprises contacting the workpiece with a metal working composition comprising a lubricating base containing extreme pressure improving amounts of a compound of the formula:

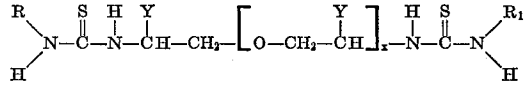


wherein R and R_1 are selected from the group consisting of hydrogen, alkyl and alkenyl, Y is hydrogen or lower alkyl and x is a number from 1 to 10.

2. The method of claim **1** wherein the metal working composition comprises a compound wherein R and R_1 are methyl, Y is methyl and x is a number from about 3 to 6.

3. The method of claim **1** wherein the metal working composition comprises a compound wherein R and R_1 are ethyl, Y is methyl and x is a number from about 3 to 6.

4. A metal working composition comprising a major amount of an aqueous lubricating base and a minor amount of a compound of the following formula sufficient to impart extreme pressure properties to said composition:



wherein R and R_1 are selected from the group consisting of hydrogen alkyl and alkenyl in which alkyl and alkenyl have up to 8 carbon atoms, Y is hydrogen or lower alkyl and x is a number from 1 to 10.

5. The composition of claim **4** wherein R and R_1 of the extreme pressure agent are methyl, Y is methyl and x is a number from about 3 to 6.

6. The composition of claim **4** wherein R and R_1 of the extreme pressure agent are ethyl, Y is methyl and x is a number from about 3 to 6.

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WARREN H. CANNON, Primary Examiner

U.S. Cl. X.R.

252—49.5