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METAL WORKING LUBRICATING COMPOSITIONS

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This invention relates to aqueous emulsions particularly suitable for use in numerous industrial metal-working processes such as metal drawing, rolling, stamping, forging, cutting, and the like. These lubricants are especially valuable for cold drawing of wire, rod, tubing and shapes.

Problems encountered in lubricating metals under conditions of the uses referred to above, are particularly complex because of the various factors encountered, such as high temperature, high pressure, presence of foreign bodies or contaminants, and the like. To effectively lubricate under these adverse conditions, the lubricant must act both as a lubricant and, in some cases, as a coolant.

In the field of metal drawing and rolling, conventional lubricants, therefore, such as palm oil, black oil or lubricating compositions containing soaps, graphite, lime and the like have serious drawbacks and difficulties are encountered in their use in that these generally available lubricants are incapable of withstanding high pressures and at the same time providing satisfactory lubrication; this results in scoring and wear of the metal being worked. Die wear is also excessive. Additionally, various lubricants, such as oils and greases, have a tendency to stain metals and/or to cause metal pick-up, or are difficult to apply to the metal surface being treated, and even more difficult to remove therefrom after being worked.

To meet the requirements demanded of a good metal-fabricating lubricant of the above class, such lubricant must have as essential properties: high film strength, ability to reduce friction and prevent welding, ability to wet the metal surface being worked and to adhere thereto, ability to produce a good surface finish, property of easy application and removal, and freedom of causing staining or discoloration; the lubricant must also have good stability and the property of causing fines, abrasives and the like to settle and separate out of the lubricating system.

It is an object of this invention to provide an improved metal-working lubricant which meets more satisfactorily the above requirements. It is another object of this invention to provide a lubricant for metal working which is stable and non-corrosive. Still another object of this invention is to provide a metal-working lubricant having the property of resisting displacement from metal surfaces. Furthermore, it is an object to provide a metal-working lubricant which is non-staining and which can be easily applied and removed from lubricated surfaces. A more specific object is to provide an improved lubricant for use in the working of stainless steels.

It has now been discovered that an excellent metal-working lubricant can be provided by forming an aqueous emulsion containing as the active ingredients a viscous hydrocarbon having a viscosity in centistokes of at least 350 or 400 at 210° F., and preferably above 700 centistokes at 210° F., an emulsifier, preferably cationic in character, a metal reactive extreme pressure agent and a mineral filler, said active ingredients being dispersed in water in certain amounts as will be hereinafter fully set forth. An excellent metal-working lubricant of this

invention can be prepared by forming: (A) an organic mixture comprising (1) a heavy hydrocarbonaceous material of which a bitumen is preferred, (2) an emulsifier, preferably cationic, e. g., an amine salt and (3) an extreme pressure agent, preferably one capable of reacting with contacting metals being worked such as extreme pressure agents capable of releasing chlorine: said three active materials being so proportioned that the bitumen constitutes the major part of said mixture and the viscosity of the total mixture is between 500 and 2000 centistokes at 210° F. and preferably between 700 and 1000 centistokes at 210° F. and (B) a slurry comprising a mixture of water and a mineral filler: said mixtures of (A) and (B) being admixed in such proportions as to form a stable emulsifiable concentrate, preferably in the ratio of from 1:1 to 1:5 respectively, which concentrate can be used as the metal working lubricant or diluted with from 1 to 20 parts of water and used as a lubricant.

GROUP A MIXTURE

Viscous or heavy hydrocarbon materials

The viscous or heavy hydrocarbon material having a viscosity in centistokes of at least 350 at 210° F. can be a natural viscous hydrocarbon such as viscous distillate or residue petroleum fraction, a bitumen (which is preferred) or a synthetic hydrocarbon such as olefinic polymers exemplified by polyisobutylene and the like, or mixtures thereof.

Bitumen, which is preferred in making up the mixture of Group A, can be an asphaltic bitumen obtained by various means during the refinement of crude oils. The asphaltic bitumen specifically may be obtained as a residue from crude oil during the distillation process, or it may be obtained from acid tars in the treatment of lubricating oils with sulfuric acid, or it may be obtained during the deasphaltizing treatment of lubricating oils bearing petroleum fractions with solvents or deasphalting agents.

The production of asphaltic bitumen by distillation of asphaltic base crude oil or topped crude may be carried out under atmospheric pressure or under reduced pressure. The distillation of the crude is continued until the residue in the still has the desired penetration. Thus a crude-oil heated to a temperature of 40 to 50° C. is fed into an evaporator where vapors are flashed off and the residue is stripped with the assistance of superheated steam at 280 to 300° C. The residue which is the asphaltic bitumen is drawn off from the evaporator through heat exchangers where it is cooled to 160 to 180° C. and thereafter stored.

Asphaltic bitumen can be removed from residual oils by the addition of low-boiling hydrocarbons which cause the precipitation of the asphaltic materials as a lower layer containing a small amount of the solvent. Thus an oil-containing asphaltic material can be dispersed in butane and heated under pressure. The mixture may then be treated with a solvent such as propane or ethane until the asphaltic material is precipitated. The quality of the asphaltic bitumen thus produced depends upon the nature of the residual oil, the solvent used, the proportion of solvent used, conditions of deasphalting, and other factors.

Asphaltic bitumens obtained by any of the above processes as well as by any other suitable means and source may be used as the base component of the coating composition of this invention. The preferred asphaltic bitumens are those which have softening points of between about 100° and 250° F. and preferably between 100° and 150° F. The asphalts may be blown if desired, by well known processes. Straight run asphalts are particularly desirable for use in compositions of this invention;

they are exemplified by materials having the properties shown in Table I.

Table I

Spr. gr. at 77° F., min	1.024
Penetration at 77° F., 100 gr., 5 sec	21–30
Ductility at 77° F., cm., min	100
Flash point, Cleveland O. C., ° F., min	590
Softening point R and B, ° F	128
Loss on heating at 163° C., 5 hrs., percent max	0.5
Pen. of residue, percent of Orig. min	80
Soluble in CS_2, percent min	99.8
Soluble in CCl_4, percent min	99.8
Ash, percent max	0.20

The asphalt generally comprises 80% to 99% of the Group A mixture. Part or all of the asphalt can be substituted with a hydrocarbon having a viscosity of at least 350 at 210° F. centistokes and preferably between 700–1500 at 210° F. centistokes, such as olefinic polymers of high molecular weight, e. g., polybutenes, polyethylenes; copolymers of olefines and iso-olefins, copolymers of propyleneisobutylene, heavy residual mineral oils, viscous lube oil extracts, and the like.

Emulsifiers

The type of emulsifiers suitable for use in lubricating emulsions are of the type which promote the formation of oil-in-water emulsions and preferably are cationic in character, exemplified by salts of high molecular weight amines and organic acids of low molecular weight; fatty alkylolamine condensation products, aliphatic amides, esters of high molecular weight fatty acids and alkylolamines, and the like. Examples of cationic emulsifiers particularly suitable in compositions of this invention include tetradecylammonium acetate, hexadecylammonium acetate, octadecylammonium acetate, octadecylammonium propionate, rosin ammonium butyrate: dodecyltrimethylammonium chloride, octadecyltrimethylammonium chloride, octadecylammonium phosphate, cetyldimethylethylammonium bromide, octadecyldimethylbenzylammonium chloride, stearamide of diethylene triamine, and the like. Preferred are the oil-soluble alkylamine salts of low molecular weight acids, e. g., octadecylammonium acetate or chloride, oleylammonium acetate, octadecylammonium propiontate, hexadecylammonium butyrate, N-octadecylpiperidinium acetate, octadecylcyclohexylammonium acetate, octadecylammonium naphthenate, octadecylammonium petroleum sulfonate, etc.

The emulsifiers can be added to compositions of this invention in from 0.5 to 15% by weight based on the final blend.

Extreme pressure agent

The extreme pressure agents must be selected from the class which are chemically reactive with metals being worked, thereby forming protective films thereon which resist rupture under extreme stresses and pressures. Compounds of this class include halohydrocarbon compounds, haloorgano phosphorus compounds, e. g., thiophosphates, phosphonates; sulfurized hydrocarbons, sulfurized fats, sulfurized fatty acids, sulfurized esters and the like; phosphorus-halogen-containing organic compounds, phosphorus - halogen - sulfur - containing compounds, and the like. Examples of compounds which are particularly applicable in compositions of this invention include dibutyl trichloromethanephosphonate, monobutyl trichloromethanephosphonate, monoisopropyl trichloromethanephosphonate, di(2-ethylhexyl) amine salt or octadecylamine salt of monobutyl trichloromethane phosphonate or its amide derivative, trichloromethanephosphonic acid, monobutyl trichloromethanephosphinate, mononyl trichloromethanethiophosphonate, tri(chloroethyl)phosphite, tributyl phosphate, tributyl thiophosphate, tricyclohexyl thiophosphate, tri(chloroethyl) thiophosphite, tricresyl phosphate: chlorinated paraffin wax, "Anglomol 85," "Parapoid 16 and16S," and the like. Of the extreme pressure agents, preferred are the haloorganophosphonates and derivatives there, such as monobutyl trichloromethanephosphonate, the di(2-ethylhexyl)amine salt or the octadecylamine salt thereof and the amide derivatives of said phosphonate and the like.

The extreme pressure agent can be present in compositions of this invention in from 0.5% to 5% by weight.

Illustrative effective compositions of Group A are as follows:

	Percent
I. Unblown asphalt	89
C_{18} amine salt of monobutyl trichloromethanephosphonate	1
Octadecylammonium acetate	10
II. Unblown asphalt	85
C_{18} amine salt of monobutyl trichloromethane phosphonate	2
Hexadecylammonium acetate	13
III. Unblown asphalt	80
C_{18} amine salt of the mixtures of: Monobutyl trichloromethanephosphonate, Dibutyl trichloromethanephosphonate, Trichloromethanephosphonic acid	3
Tetradecylamine acetate	17
IV. Blown asphalt	87
Chlorinated paraffin wax (40% cl)	5
Octadecylammonium acetate	8
V. Unblown asphalt	83
Parapoid 16 [1]	5
Octadecylammonium acetate	12
VI. Unblown asphalt	89
Octadecylamine salt of monobutyl trichloromethanephosphonate	1
Octadecyltrimethylammonium chloride	10
VII. Unblown asphalt	83
Chlorinated paraffin wax (40% Cl)	5
Octadecyltrimethylammonium chloride	12
VIII. Unblown asphalt	88
Octadecylamine salt of monobutyl trichloromethanephosphonate	2
Octadecylammonium acetate	10
IX. Polybutene (1500 cs./210° F. visc.)	88
Octadecylamine salt of monobutyl trichloromethanephosphonate	8
Octadecylamine acetate	10
X. "Dutrex" [2] (lubricating oil extract)	89
Octadecylamine salt of monobutyl trichloromethanephosphonate	1
Octadecylammonium acetate	8
XI. Blown asphalt	89
Sulfurized oleic acid	1
Octadecylammonium acetate	10
XII. Blown asphalt	89
C_{18} amine salt of monobutyl trichloromethanephosphonate	1
Octadecylammonium acetate	10
XIII. Unblown asphalt	89
Anglamol 85 [3]	1
Octadecylammonium acetate	10
XIV. Blown asphalt	89
Anglamol 85 [3]	1
Octadecylammonium acetate	10

[1] Note Composition F.

[2] Softening point, °C 42.4
Sp. Gr. 20/4° C 1.072
Viscosity cs. at 210° F 292 (low)
Mol. Wt 444

[3] Note Composition D.

GROUP B MIXTURE

As stated previously, the mixture of Group B is a slurry

of water and a lubricating mineral filler which, when admixed with compositions of Group A, forms the desired concentrated lubricating composition of this invention which can be used as such or diluted with substantial amounts of water and used as a metal working lubricant.

The fillers should be non-abrasive in character and include zinc oxide, zinc sulfate, zinc sulfide, barium sulfate, talc, chalk, mica, colloidal clays, e. g., bentonites, kaolin, tungsten mono- and di-sulfide, molybdenum mono- and di-sulfide, lead oxide, basic lead carbonate, silver sulfate and the like, as well as mixtures thereof. Preferred fillers are chalk, lithopone, white lead and zinc oxide.

The amount of filler used can vary over a wide range and depends primarily upon the conditions under which lubricants of this invention are used. Generally the filler can be present in from 2 to 40% and preferably from 5 to 15% based on the final composition, that is, after the mixtures of A and B are admixed. Under mild metal working operation, the filler can be omitted, if desired.

If desired, the emulsifying agent can be added in the water phase (B) rather than in the Group A mixture and the two phases admixed under conditions mentioned above to form the final composition.

Preferred B type mixtures are: slurry of lithopone in water, zinx oxide in water, barium sulfate in water, bentonite in water, or these slurrys containing the cationic emulsifiers of Group A, e. g., octadecylammonium acetate.

The final compositions of this invention are prepared by admixing mixtures of A with B in desired proportions such as in the ratios of 1:1 or 1:5, preferably under agitating conditions, with or without the application of heat, until a stable emulsion has formed.

Illustrative examples of final concentrate emulsions of this invention which are particularly suitable for the drawing of stainless steel are:

Composition A [1]:	Percent
Unblown asphalt (Table I)	40
C_{18} amine salt of monobutyl trichloromethanephosphonate	1
Octadecylammonium acetate	5
Lithopone	30
Water	24

Composition B:	
Unblown asphalt (Table I)	38
Octadecylamine salt of monobutyl trichloromethanephosphonate	1
Lithopone	10
Octadecylammonium acetate	5
Water	46

Composition C:	
Unblown asphalt	35
C_{18} amine salt of monobutyl trichloromethanephosphonate	1
Zinc oxide	10
Octadecylammonium acetate	5
Water	49

Composition D:	
Unblown asphalt	35
"Anglamol 85" [2]	3.5
Lithopone	10
Octadecylammonium acetate	5
Water	46.5

Composition E:	
Unblown asphalt	35
Chlorinated paraffin wax (40% Cl)	5
Ditert-butyl hydroquinone	2
Lithopone	10
Octadecylammonium acetate	5
Water	43

Composition F:	
Unblown asphalt	35
"Parapoid 16" [3]	3.5
Lithopone	10
Hexadecylammonium acetate	5
Water	46.5

Composition G:	
Polybutene (1500 cs./210° F. visc.)	35
Di-2-ethylhexyl amine salt of monobutyl trichloromethanephosphonate	1
Lithopone	10
Octadecylammonium acetate	5
Water	46

Composition H:	
Unblown asphalt	35
Di-2-ethylhexyl amine salt of monobutyl trichloromethanephosphonate	1
Zinc oxide	10
Dodecyltrimethylammonium chloride	5
Water	46

Composition I:	
Unblown asphalt	38
Monobutyl trichloromethanephosphonate	2
Octadecylammonium acetate	5
Chalk	10
Water	45

[1] Compositions A to I were prepared by combining suitable mixtures from Groups A and B.

[2] Anglamol 85 : a Cl, S and P containing organic compound prepared by Lubri-Zol Corporation.

[3] Parapoid 16 : a sulfurized unsaturated fatty organic material distributed by Enjay Co., Inc.

In order to illustrate the outstanding lubricating properties which compositions of this invention possess they were subjected to the following test:

In actual plant operation, Type 304 stainless steel tubes having an initial outside diameter of 1⅛ inches were reduced about 42% in cross-sectional area by cold drawing with Carboloy dies and mandrels with the aid of lubricants as identified in the table below and the superiority of lubricants of this invention over the best known available drawing lubricant can be clearly noted.

Cold drawing of stainless steel on a drawbench

[Type 304, oxidized stainless steel tubing, 1⅛" O. D.]

Composition	Area Reduction, Percent	Drawing Speed, ft./min.	Chatter During Draw	Mandrel Pickup	Internal Scoring of tube	Total force (Lb.)	Die force (Lb.)	Mandrel force (Lb.)
B	42	18-36	None	None	None	9,400	7,700	1,700
D	42	18-36	do	do	do	9,250	7,300	1,950
F	42	18-36	do	Light	Moderate	9,000	7,150	1,850
E	42	18-36	do	None	None	7,800	5,850	1,950
H	42	18-36	do	do	do	7,800	6,100	1,700
G	42	18-36	do	do	do	9,000	6,700	2,300
Graphite	42	18	Severe	Severe, Fractured.	Severe	10,250	6,250	4,000
Bright Stock	42	Inches	Fractured	Severe	do	<11,000		

Compositions of this invention can be applied to the metal being worked by a suitable means such as brushing, dipping, spraying and the like, and the coated metal stored until ready to be worked or directly drawn on application of the lubricant.

I claim as my invention:

1. A metal-working lubricating concentrate composi-

tion containing the following constituents in the following proportions:

	Percent by weight
Unblown asphalt	35–38
Octadecylamine salt of monobutyl trichloromethanephosphonate	1
Lithopone	10
Octadecylammonium acetate	5
Water	49–46

2. A metal working lubricating concentrate composition containing the following constituents in the following proportions:

	Percent by weight
Unblown asphalt	50
C_{18} amine salt of monobutyl trichloromethanephosphate	1
Octadecylammonium acetate	5
Lithopone	30
Water	24

3. An oil-in-water emulsion containing the composition of claim 2 and additional water in the ratio of from 1 to 1 to 1 to 20, respectively.

4. A metal working lubricant concentrate containing: (A) from 80% to 90% of unblown asphalt, from 0.5% to 5% of an oil-soluble alkylamine salt of monobutyl trichloromethanephosphonate, selected from the group consisting of octadecylamine salt of monobutyl trichloromethanephosphonate and di-2-ethylhexylamine salt of monobutyl trichloromethanephosphonate, and from 0.5% to 10% of an oil-soluble alkyl ammonium acetate, selected from the group consisting of hexadecylammonium acetate and octadecylammonium acetate; and (B) a water slurry containing from 2% to 40% of a non-abrasive inorganic lubricating filler, the ratio of (A) to (B) ranging from 1:1 to 1:5, respectively.

5. A metal working lubricant concentrate containing: (A) from 80% to 90% of unblown asphalt, from 0.5% 5% of octadecylamine salt of monobutyl trichloromethanephosphonate and from 0.5% to 10% of octadecylammonium acetate, and (B) a water slurry containing from 2% to 40% of a non-abrasive inorganic lubricating filler, the ratio of (A) to (B) ranging from 1:1 to 1:5, respectively.

6. A metal working lubricant concentrate containing: (A) from 80% to 90% of unblown asphalt, from 0.5% to 5% of octadecylamine salt of monobutyl trichloromethanephosphonate and from 0.5% to 10% of octadecylammonium acetate and (B) a water slurry containing from 5% to 15% of lithopone, the ratio of (A) to (B) ranging from 1:1 to 1:5, respectively.

References Cited in the file of this patent

UNITED STATES PATENTS

1,440,356	Morrell	June 22, 1920
1,952,973	Craig	Mar. 27, 1934
2,256,877	Bertsch	Sept. 23, 1941
2,466,647	Stern	Apr. 5, 1949
2,552,913	Waugh	May 15, 1951

OTHER REFERENCES

Vol. 35, page 127, Industrial and Engineering Chemistry.