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METAL WORKING LUBRICANT

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This invention relates to novel lubricants and methods of making them. More particularly, this invention pertains to metal-working or metal-fabrication lubricants for use in rolling, drawing, deep drawing, rod and tube drawing, forging of metals and the like.

Problems encountered in lubricating metals under conditions of the uses referred to in the previous paragraph are particularly complex because of the various factors encountered, such as high temperature, excess pressure, emulsification, presence of foreign bodies or contaminants, work speeds and the like. To effectively lubricate under these adverse conditions, the lubricant must act primarily as a coolant and as a lubricant.

In the field of rolling lubricants, palm oil has been considered to be most efficient and suitable for use in connection with the heavier metals such as iron and its alloys, steels. However, palm oil has serious drawbacks, particularly in some applications, in that it is difficult to remove from metal surfaces thereby requiring the use of cleaners, which greatly increases operating cost. Also, it has a tendency to stain some metal surfaces which on annealing mars the surface and exerts a detrimental effect when such metals are to be subsequently tinned, coated and the like. In addition, metal surfaces which become too heavily coated with palm oil cause excessive slippage of the rolls thereby decreasing rolling efficiency. Palm oil is not always readily available; hence, a cheap and effective substitute for it is greatly desired.

To meet the requirements demanded of a good metal-fabricating lubricant, such as a roll lubricant, it must have as essential properties: film strength, ability to reduce friction, ability to wet metals in presence of water, ability to produce a good lustre on metal surface worked, ease of removal and non-staining and de-emulsifying properties, i. e., separating from water and contaminants, including fines.

FILM STRENGTH

When lubricated metal surfaces are forced to slide past each other under high pressures, there is a tendency for surface asperities to penetrate the lubricant film and the penetrating metal to adhere to the opposing metal surface; this permits the transfer of metal from one surface to another. This phenomenon, known in metal-working operation as "pick-up" of the worked metal by the die or roll, may become very pronounced at elevated temperatures. Although high temperatures may be a result of high friction and may lead to "pick-up," it is generally agreed that the ability of a lubricant to prevent adhesion of metal surfaces is a property distinct from and not necessarily related to ability of the

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lubricant to reduce friction between sliding surfaces which do not adhere. For this reason, the ability of a lubricant to form surface films which prevent actual metal-to-metal contact and adhesion is very essential.

REDUCTION OF FRICTION

Roll lubricants must possess the ability to reduce friction between the rolls and the work sheet in order to reduce power consumption, increase reduction per pass and give a lower limit to the metal thickness, prevent overheating and minimize the force which must be applied to the rolls. The property of a lubricant to reduce friction is referred to loosely as "oiliness" and depends upon the sheer strength of the film formed on a metal surface and to the rheological behavior of thin films of oil when subjected to high pressures.

WETABILITY AND ADHESION

Since roll lubricants are usually used in conjunction with water as a coolant, they must possess the property of displacing water from metal surfaces and resist the washing action of large quantities of water applied to the rolls and work sheet. Often washing water is applied in the form of a high pressure stream so that the ability of the lubricant to adhere to metal surfaces is of paramount importance.

LUSTRE

The appearance of the surface of rolled stock referred to in practice as "lustre" is markedly influenced by the character of the roll lubricant. To accomplish this, lubricants used for this purpose should prevent microscopic tears on the worked metal surface.

EASE OF REMOVAL AND NON-STAINING

A serious drawback of ordinary oils is the difficulty of removing them from rolled metal sheets. Electrolytic cleaners are sometimes used to remove the oil for if it is left on the metal surface and the metal is thereafter annealed, the metal surface becomes stained. Roll lubricants should, therefore, possess the property of being easily removed when desired and also not stain the surface with which it is in contact, regardless of the temperature. Ordinarily, in the case of aluminum the lubricant is selected so that it will evaporate from the surface during annealing operations, and it is desired that it evaporate without staining.

CORROSION RESISTANT

Efficient roll lubricants in addition to being able to withstand high temperature and pressure must be non-corrosive during the rolling process and preferably act as a corrosion inhibitor after the rolling process, particularly in cases where the rolled metal is stored for long intervals before being further worked.

It is an object of this invention to provide an improved metal-rolling lubricant. 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 tacky metal-working lubricant having the property of resisting water displacement from metal surfaces. Furthermore, it is an object to provide a metal-working lubricant which is non-staining and which can be easily removed from lubricated surfaces. A more specific object is to provide an improved lubricant for use in the working of aluminum, stainless steel and other metals and alloys.

It has now been discovered that a metal-working lubricant such as a rolling lubricant having outstanding properties can be prepared by forming a blend of a waxy hydrocarbon, substantially non-aromatic and a polymeric olefin, waxy hydrocarbon comprising at least 80% and preferably 85 to 95% of the blend, said blend having admixed therein as a primary ingredient from about 3% to about 10% and preferably from about 3% to 6% of a halo-organic compound such as halo waxes, halo-fatty acids and esters thereof and the like.

Waxy materials can be recovered from residuum lube oil fractions, and these wax fractions can be split still further into special wax cuts having desired characteristics by use of selective solvents. This is based on a difference in solubility of different waxy fractions in a given solvent. Thus, when using a methylethyl ketone type solvent, the aromatic constituents can be removed by successively cooling the mixture down to between about −40° F. and −76° F. so as to remove the aromatics which remain substantially soluble in the solvent as the temperature is lowered, while the straight-chain waxes and isoparaffins become substantially insoluble in the solvent. The straight-chain waxes can be separated from the isoparaffins by extraction and fractional crystallization.

The above type of waxy hydrocarbons may be admixed with synthetic waxes produced by polymerization of olefins under pressure or by dehydrating long-chain fatty alcohols such as octadecyl alcohol and the like. Admixed with non-aromatic waxy hydrocarbon may be minor amounts of waxy materials obtained from non-hydrocarbon services such as marine or animal waxes, vegetable waxes and the like, and specifically may be illustrated by spermaceti, Japan wax, carnauba wax, montan wax, sugar cane wax, cotton wax, etc., and the mixture oxidized.

The other constituent of the base blend is a polymeric unsaturated hydrocarbon and may be mono- and/or polyolefinic and/or acetylenic hydrocarbons, which may, if desired, have attached polar groups, said polymeric materials being of rather high molecular weight such as above 300 and preferably above 1,500 and may even be within the limits of 5,000 or 10,000 or even higher, such as 100,000 or 500,000, etc.

These olefinic products may be obtained from various sources and by various means. Thus, olefins may be obtained by hydrogenation of paraffins, such as by the cracking of paraffin waxes, or by the dehalogenation of alkyl halides and the like. Also, as olefinic starting materials for the production of such polymers, individual olefins or mixtures of olefins and non-olefinic hydrocarbons may be used. Starting materials may

be butylenes, amylenes, refinery gases containing normally gaseous olefins and cracked distillates or other relatively low-boiling hydrocarbon mixtures containing normally liquid olefins, and mixtures of normally liquid olefins containing dissolved therein normally gaseous olefins. Polymers resulting from the treatment of monoolefins preferably iso-monoolefins such as isobutylene and isoamylene and/or copolymers obtained by the polymerization of hydrocarbon mixtures such as isoolefins and normal olefins may be used. The polymerization of these olefins and their mixtures may be obtained by use of suitable catalysts such as Friedel-Crafts type and the like.

Examples of olefinic and/or acetylinic hydrocarbons which may be obtained from any source and utilized in forming the desired sulfurized products of this invention are ethylene, propylene, butene-1, butene-2, isobutylene, the amylele, hexene-1, 4-methyl-pentene-1, 4,4-dimethyl-pentene-1, 4-methyl-pentene-2, octene-1, decene-1, cetene-1, styrene, cyclohexene, 3-methylcyclohexene, 1,4-diphenyl, butene-2, butadiene-1,3, pentadiene-1,3, pentadiene-1,4, hexadiene-1,5, hexadiene-1,4, pentadecene-8, heptadecene, hexadecene-1, tridecene-7, nonadecene-10, 3,9-diethyltridecene-6, dodecene-1, triacontene-14, pentatriacontene-17, olefins, obtained by decarbonylation of oleyl alcohol or such unsaturated alcohols as are obtained by carboxyl reduction of sperm alcohol, olefins obtained by dehydration of high molecular weight saturated alcohols, etc., acetylene, propyne, butyne-1, pentyne-2, hexyne-1, cetyne-1, octyl acetylene, phenyl acetylene, etc., and their homologues and analogues.

Copolymers of olefins and non-aromatic hydrocarbons may also be used. The olefins which may be used to form the copolymers of this type include isobutylene, 2-methylbutene-1,2, ethylbutene-1, secondary and tertiary amylenes, hexylenes and the like. The non-aromatic hydrocarbons may include butadiene, isoprene, cyclopentadiene, 2,3-dimethylbutadiene-1,3, pentadiene-1,3, hexadiene-2,4, the substituted diolefins such as diisobutenyl; the acetylenes such as acetylene, vinyl acetylene and the like.

The copolymerization is preferably carried out in the presence of a Friedel-Crafts type catalyst and in the presence of a suitable diluent such as liquified ethylene, propane and the like.

The catalysts which may be employed during the polymerization reaction may be any Friedel-Crafts catalyst such as are listed by Calloway in Chemical Review 17, 327 (1925). The polymerization may be carried out at low temperatures such as below zero degrees centigrade, or at elevated temperatures such as above 50° C. and 100° C. and higher.

Among the most preferred polymeric materials suitable for use in compositions of this invention are:

Polyisobutylene polymer (mol. wt. 1,500–5,000)
Polyethylene polymer (mol. wt. 1,000–10,000)
Polybutenes (mol. wt. 5,000–6,000)
Copolymer of isobutylene and ethylene (mol. wt. 1,500–10,000)
Copolymer of propylene and isobutylene (mol. wt. 500–10,000)
Copolymer of butadiene and isobutylene (mol. wt. 15,000–20,000)

The friction reducer or oiliness agents which form an integral part of compositions of this invention are halo organic compounds such as halogenated paraffin wax, halogenated cracked wax olefins, halogenated fatty acids having at least 8 and preferably 12 to 24 carbon atoms in the molecule, esters of said fatty acids and the like. The halo radical or radicals may be chlorine, bromine, fluorine, and/or iodine. Agents which are specifically preferred are chlorinated paraffin wax, chlorinated cracked wax, chlorinated foots' oil, olefin of C_{10}–C_{24}, chlorinated synthetic rubber, chloro-bromo-paraffin wax, dichlorostearic acid, dichloro-oleic acid, methyl dichloro-stearate, butyl dichloro-stearate, polybromostearic acid, methyl polybromostearic acid, methyl dichloro-ricinoleate, chlorinated waxy esters, e. g., beeswax, montan wax, and the like.

Highly desirable metal-working lubricants such as rolling and drawing lubricants can be prepared by using formulations within the following range:

Material	Amount
	Percent
Base blend:	
1. Waxy hydrocarbon	80–95 } 97–89
2. Polymeric material mol. wt. 300–500,000 and preferably 1,500–5,000	20–5 }
Primary Additive:	
3. Halo-organic compound, e. g., chlorinated paraffin wax or methyl dichloro-stearate, etc.	2–10
Secondary or optional Additives:	
4. Amines, sulfonates, etc	0–1

Specific compositions of this invention are:

Composition A

	Per cent
Methyl dichlorostearate	3
Polybutene (mol. wt. 8,000–10,000)	10
Soft wax residue (M. P. 39°–40° C.)	Balance

Composition C

	Per cent
Dichlorostearic acid	10
Polyisobutylene (mol. wt. 1,500–10,000)	5
Residue petrolatum	Balance

Composition E

	Per cent
Methyl dichlorostearate	3
Sulfurized sperm oil	1
Polyisobutylene	5
Soft wax obtained from residue petrolatum (M. P. 40° C.)	Balance

Composition F

	Per cent
Chlorinated paraffin wax	3
Polybutene (mol. wt. 8,000–10,000)	5–10
Residue petrolatum	Balance

Table I below further illustrates compositions of this invention:

Table I

	1	2	3
Primary Additive:			
methyl dichlorostearate	------	------	------
dichlorostearic acid	------	x	x
chloro-paraffin wax	x	------	------
chloro-beeswax	------	------	------
Secondary Additive:			
Sulfurized sperm oil	------	------	x
oleic acid	x	------	------
butyl ricinoleate	------	x	------
Base Blend:			
(*a*) Waxy hydrocarbon—			
n-paraffin wax	------	------	------
petrolatum	------	------	------
residual wax	x	x	x
(*b*) polymeric material—			
polyethylene	x	------	------
polybutene	------	x	x
copolymer of isobutylene-propylene	------	------	------

x=amount of material used and can be varied within the ranges disclosed in column 5.

To illustrate the pronounced improvement obtained with compositions of this invention, a number of these compositions were subjected for test in the four-ball wear machine under conditions indicated in Table II.

Table II

[Average results of one-minute friction tests at 1300 R. P. M. with 18–8 stainless-steel discs rubbed by a hard steel ball, 15 kg. load.]

Composition	30° C.		80° C.		130° C.	
	D	μ	D	μ	D	μ
Composition A	------	------	.70	.042	.69	.045
Composition F	------	------	.65	.041	.67	.040
Composition X[2]	------	------	2.1	.16	[1]——	——
Composition Y	------	------	1.5	.101	——	——
Composition Z	2.2	.25	——	——	——	——

D=Scar diameter, mm.
μ=Coeff. of friction, average of values at 30, 40, 50 and 60 seconds.
[1] —— =seizure.
[2] Compsition X=10% polybutene in residue petrolatum.
Composition Y=10% oleic acid + 3% chlorinated paraffin wax in paraffin wax.
Composition Z=1% tricresyl phosphate in mineral oil.

In conjunction with compositions of this invention, minor amounts, generally less than 1%, of other additives can be added, if desired, in order to fortify the compositions, such as:

A. High molecular weight fatty acids derived from animal, vegetable, marine oils, e. g.,
1. Animal oil:

tallow	neat's foot
lard	wool fat
bone	horse foot oils, etc.

2. Vegetable oils:

castor	corn
cashew	cottonseed
peanut	kapok
cocoanut	rapeseed
jojoba seed	ravison
olive	sesame
olive kernel	sunflower
palm oil	teaseed oils, etc.
palm kernel oils	

3. Marine oils:

codfish	porpoise body and jaw oils
codliver	salmon oil
dogfish	sardine and sardine liver oils
dolphin body	seal oil
dolphin fish	shark and shark liver oils
herring	sperm whale body and head oils
japfish	whale oil, etc.
menhaden	

B. Natural-occurring fatty acids of high molecular weights:
1. Saturated:

capric	stearic
undecylic	arachidic
lauric	lignoceric
myristic	cerotic
palmitic	montanic acids, etc.

2. Unsaturated:

oleic	linolenic
linoleic	brassidic
erucic	elaidic acids, etc.

3. Substituted fatty acids:
ricinoleic
ricinelaidic
hydroxystearic acids, etc.

C. Esters of any of the above acids with mono- and polyhydric alcohols and other types of esters, e. g.,
1. Glycerol mono-oleate, methyl dichlorostearate, diglycol stearate, di-2-ethyl hexyl-azelate, n-decyl hydrogen phthalite or succinate, octadecyl stearate.
2. Esters of inorganic acids, e. g., phosphatidic materials such as cephalin and lecithin.

D. Sulfur-containing materials, e. g.,
dibenzyl disulfide
sulfurized sperm oil
sulfurized cottonseed oil
sulfurized fatty acids as listed under part B

Rolling lubricants of this invention are well adapted as rust inhibitors after the rolled sheet has been worked.

The roll lubricant of this invention may be applied to the rolls of a sheet metal rolling mill by any suitable means such as spraying, dripping, or the like. It may be applied to the sheet metal prior to or during rolling.

In addition to being an excellent roll lubricant, compositions of this invention may be used as drawing lubricants, forging and die lubricants and in various other processes where drawing and working of metals requires lubrication.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, the invention, however, is not to be limited thereto or otherwise restricted except by the prior art and the scope of the appended claims.

The invention claimed is:

1. A metal-working lubricant consisting essentially of a base blend of a soft residue wax and an olefinic hydrocarbon polymer having a molecular weight above 300, said soft residue wax constituting at least 80% of the blend and the polymer constituting essentially the remainder of said blend, and having incorporated in said base blend from 2% to 10% based on the total lubricant, of a halogenated extreme pressure compound selected from the group consisting of halogenated wave, halogenated high molecular weight fatty acids, and hologenated esters of said fatty acids.

2. A metal-working lubricant consisting essentially of the following components in the specified proportions:

	Per cent
Methyl dichlorostearate	3
Polybutene (mol. wt. 8,000–10,000)	10
Solt wax residue (M. P. 39–40° C.)	Balance

3. A metal-working lubricant consisting essentially of the following components in the specified proportions:

	Per cent
Chlorinated paraffin wax (40% Cl.)	3
Polybutene (mol. wt. 8,000–10,000)	5–10
Soft residue wax	Balance

4. A metal-working lubricant consisting essentially of the following components in the specified proportions:

	Per cent
Methyl dichlorostearic acid	3
Oleic acid	1
Polyisobutylene	5
Soft residue wax	Balance

5. A metal working lubricant consisting essentially of the following components in the specified proportions:

	Per cent
Methyl dichlorostearate	3
Sulfurized sperm oil	1
Polyisobutylene	5
Soft residue wax	Balance

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