

## UNITED STATES PATENT OFFICE

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## METALWORKING LUBRICANT

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1

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, forging of metals and the like.

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

In the field of rolling lubricants, palm oil was considered most efficient and suitable. However, palm oil has serious drawbacks in that it is difficult to remove from metal surfaces thereby requiring the use of cleaners which greatly increase operating cost. Also, it has a tendency to stain surfaces which on annealing mars the surface and exerts a detrimental effect when such metals are to be subsequently tinned, alloyed 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 also costly, and a cheaper and effective substitute for palm oil as a metal working lubricant is greatly desired.

To meet the requirements demanded of a good metal fabricating lubricant such as a roll lubricant, it must have high adsorption properties to adhere or wet metal surfaces even in the presence of water. Also enough reduction of friction coefficient must be realized to keep the mill from overheating.

Essential properties of such lubricants are: 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.

*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 adhere; this in turn 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 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.

2

*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, prevent overheating and minimize the force which must be applied to the rolls. The property of a lubricant to reduce friction is referred to as "oiliness" and depends upon the shear strength of the film formed on a metal surface and on the rheological behavior of thin films of oil when subjected to high pressures.

*Wettability 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 spray 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 be non-staining and prevent microscopic tears on the worked metal surface.

*Ease of removal and non-staining*

A serious drawback of palm oil is the difficulty of removing it from rolled metal sheets. Generally electrolytic cleaners are required to remove the palm 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.

*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 roll lubricant substantially superior to palm oil. 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 being displaced by water sprayed under pressure. Furthermore, it is an object of this invention to provide a metal working lubricant which is non-staining and which can be easily removed from lubricated surfaces.

It has now been discovered that a metal working lubricant such as a rolling lubricant having outstanding properties can be prepared by blending into an acid-treated light liquid hydrocarbon having a boiling point not exceeding the gas oil range, as the primary ingredient from 3 to 10% and preferably 4 to 7% of a fatty material or derivative thereof selected from the class consisting of lanolin, olein and ocnol. If desired, specific types of secondary additives can be admixed into the above blend of acid-treated light oils, e. g. an acid-treated gas oil and fatty materials, said secondary additives being selected from organic amines, alkylated phenolic compounds and salts of organic acids. The secondary additives, if used in compositions of this invention, are added in amounts generally not exceeding 0.01% to 0.5% by weight.

The light hydrocarbons having a boiling range of from about 300° F. to about 700° F. and preferably boiling within the range of from about 400° F. to about 650° F. may be acid-treated in a variety of ways. Thus, such fractions which may be straight-run, thermally and/or catalytically cracked hydrocarbons such as gas oil may be treated with sulfuric acid, or other acids such as phosphoric and hydrochloric acids or mixtures thereof followed by neutralization of separated sour oil phase by use of aqueous alkali. The process may be modified by subjecting the acid-treated oil to a clay treatment, mild oxidation and the like.

The preferred method of acid-treating the base oils used in compositions of this invention is to acid-treat with 3 to 30 pounds and preferably with 6 to 20 pounds of about 87-95% sulfuric acid per barrel of oil. The amount and strength of acid used depend upon the base oil's source, its boiling range and whether it is a straight run, thermally cracked or catalytically cracked stock. For a Mid-Continent or West Texas stock boiling within the gas oil range, between about 6 and about 20 pounds of 93% sulfuric acid is required in order to obtain a desired acid-treated oil for metal working.

The sludge which is formed from the above acid treatment is allowed to settle and is removed. The sour oil is then carefully neutralized with aqueous caustic solution and/or a lime solution. The aqueous solution is then withdrawn and the oil is then given a clay treatment. Any of the various adsorptive clays, e. g. fuller's earth, Attapulgas or any aluminate silicate clays, well known in the art may be utilized. If desired, the oil may be mildly oxidized during the clay treatment by blowing with oxygen or air at about 120-135° F.

The properties of a Mid-Continent gas oil before and after being acid-treated (20 lbs. 93% H<sub>2</sub>SO<sub>4</sub>/bbl.), neutralized and clay (Attapulgas) treated is given in the table below:

|                      | Mid-Cont.<br>Gas Oil | Acid-treated<br>Mid-Cont.<br>Gas Oil |
|----------------------|----------------------|--------------------------------------|
| Gravity °API.....    | 36.7                 | 35.3                                 |
| Color, NPA.....      | 114+                 | 1                                    |
| Flash, O. C. °F..... | 184(CC)              | 310                                  |
| Pour, °F.....        | 10                   | 15                                   |
| Cloud, °F.....       | 20                   | 28                                   |
| ASTM, dist.:         |                      |                                      |
| IBP, °F.....         | 490                  | 544                                  |
| 10%.....             | 550                  | 560                                  |
| 50%.....             | 565                  | 572                                  |
| 90%.....             | 592                  | 592                                  |
| FBP, °F.....         | 625                  | 624                                  |

Compositions of this invention are obtained by blending into acid-treated oils as described above, minor amounts of a primary additive selected from the classes including lanolin, olein and ocnol, the latter being a technical grade oleyl alcohol. If desired, the blends thus obtained may be mildly oxidized by either blowing with oxygen or air or allowing the blend to be exposed to the atmosphere for about a week or ten days at a temperature of from 135 to 250° F. and preferably at 200° F.

Of the primary additives referred to above, lanolin and particularly anhydrous lanolin are most preferred because of its wide applicability in various metal working operations in compositions of this invention. An anhydrous lanolin suitable for use in compositions of this invention has the following properties:

|                                                    |      |
|----------------------------------------------------|------|
| Neutralization No .....                            | 148  |
| Iodine No .....                                    | 45   |
| Free fatty acid, per cent (ASTM<br>method B) ..... | 0.74 |
| Water .....                                        | None |

In rolling operations and particularly in the cold rolling of aluminum sheets, staining due to the lubricant used is a serious problem. Although compositions of this invention reduce staining to a minimum, it has been found that this factor can be substantially entirely eliminated by addition to compositions of this invention minute amounts of metallic naphthenates and/or oleates or by addition of an alkylated phenol or organic amine. The addition of these secondary additives acts as excellent stain-suppressors when added in amounts of from 0.01 to 1%. The stain-suppressors particularly preferred are the Ca, Mg, Ba, Sr, Cu, Zn, Co, Mn, Al, Pb naphthenates and/or oleates; the alkylated phenols, e. g. 2,4-dimethyl-6-tertiary butyl phenol, 2,4-dibutyl-6-methyl phenol; 2-ethyl-4-octyl phenol; C<sub>14</sub> alkylated cardanol, octyl phenol, etc. Among the organic amines which can be used as stain-suppressors are diphenylamine, phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, octyl amine, octadecyl amine, etc.

Specific examples of compositions of this invention are:

|                                                                                 | Per cent |
|---------------------------------------------------------------------------------|----------|
| Composition A:                                                                  |          |
| Lanolin .....                                                                   | 4-6      |
| Acid-treated gas oil .....                                                      | Balance  |
| Composition B:                                                                  |          |
| Ocnol .....                                                                     | 4-6      |
| Acid-treated gas oil .....                                                      | Balance  |
| Composition C:                                                                  |          |
| Olein .....                                                                     | 4-6      |
| Acid-treated gas oil .....                                                      | Balance  |
| Composition D: Oxidized mixture of acid-treated gas oil containing 4-6% lanolin |          |
| Composition E:                                                                  |          |
| Lanolin .....                                                                   | 4-6      |
| Ca naphthenate .....                                                            | 0.6-0.8  |
| Acid-treated gas oil .....                                                      | Balance  |
| Composition F:                                                                  |          |
| Lanolin .....                                                                   | 3-6      |
| Cu naphthenate .....                                                            | 0.3      |
| Acid-treated gas oil .....                                                      | Balance  |
| Composition G:                                                                  |          |
| Ocnol .....                                                                     | 3-6      |
| Ca naphthenate .....                                                            | 0.6-0.8  |
| Acid-treated gas oil .....                                                      | Balance  |

5

|                                             |          |
|---------------------------------------------|----------|
| Composition H:                              | Per cent |
| Lanolin                                     | 3-6      |
| 2,4 ditertbutyl-6-methylphenol <sup>1</sup> | 0.6-0.8  |
| Acid-treated gas oil                        | Balance  |

|                                |         |
|--------------------------------|---------|
| Composition I:                 |         |
| Ocenol                         | 3-6     |
| 2,4 ditertbutyl-6-methylphenol | 0.3-0.8 |
| Acid-treated gas oil           | Balance |

|                      |         |
|----------------------|---------|
| Composition J:       |         |
| Lanolin              | 3-6     |
| Diphenylamine        | 1       |
| Acid-treated gas oil | Balance |

<sup>1</sup> The alkyl phenol can be dispersed into about 2% of a heavy oil (500 SUS at 100° F.) and this mixture is blended into the composition.

The following table further illustrates compositions of this invention:

|                                                   | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---------------------------------------------------|---|---|---|---|---|---|---|---|---|----|
| Primary Additives:                                |   |   |   |   |   |   |   |   |   |    |
| Lanolin                                           | x | x | x |   |   | x | x |   | x |    |
| Ocenol                                            |   |   |   | x |   |   |   | x | x |    |
| Olein                                             |   |   |   |   | x | x |   |   |   | x  |
| Secondary Additives:                              |   |   |   |   |   |   |   |   |   |    |
| Cu naphthenate                                    | x |   |   | x |   |   |   | x | x |    |
| Co naphthenate                                    |   |   |   |   |   |   | x | x |   |    |
| Pb naphthenate                                    |   | x |   |   |   |   |   |   | x |    |
| Ca oleate                                         |   |   | x |   | x |   |   |   |   |    |
| 2,4-ditertbutyl-6-methyl phenol                   | x | x |   |   |   |   | x |   |   |    |
| 2,4-dimethyl-6-tertbutyl phenol                   |   |   | x |   |   |   |   | x |   |    |
| octyl phenol                                      |   | x | x |   | x |   | x | x |   |    |
| Base:                                             |   |   |   |   |   |   |   |   |   |    |
| Acid-treated gas oil                              | x | x | x |   | x |   | x | x |   |    |
| Acid-treated hydrocarbon distillate (500-600° F.) |   |   |   | x |   |   |   |   |   |    |
| Oxidized acid-treated gas oil                     |   | x |   |   |   | x |   |   | x | x  |

To illustrate the pronounced improvement obtained from compositions of this invention, a number of these compositions were subjected for test in the Four-ball Wear Tester and the compositions were compared with other compounded rolling lubricants.

[Condition of test: rotating steel top ball, 3 aluminum discs, One minute, 680 R. P. M., 7 kg. load, 75° F.]

|                                                    | Coefficient of friction |
|----------------------------------------------------|-------------------------|
| Non-acid-treated gas oil                           | 0.137                   |
| Acid-treated gas oil                               | 0.106                   |
| Composition A                                      | 0.025                   |
| Composition B                                      | 0.029                   |
| Composition D                                      | 0.029                   |
| Composition 9                                      | 0.029                   |
| Composition 2                                      | 0.020                   |
| Composition 10                                     | 0.021                   |
| Composition A (using non-acid-treated gas oil)     | 0.062                   |
| Composition B (using non-acid-treated gas oil)     | 0.083                   |
| Composition X (gas oil containing 2% stearic acid) | 0.157                   |
| Composition Y (gas oil containing 2% lecithin)     | 0.102                   |
| Composition Z (gas oil containing 5% linseed oil)  | 0.098                   |

Compositions of this invention were also subjected to the Alcoa Stain test which comprises placing 1 ml. of the material being tested on a polished 5"x5" aluminum plate and heating in an electric furnace at 650° F. for 30 minutes. The plate is then examined for staining and is rated as follows:

- A—stain free
- B—light stain
- C—medium stain
- D—dark medium stain
- E—dark stain

6

The results of compositions tested were as follows:

| Composition:                                                                        | Staining rating |
|-------------------------------------------------------------------------------------|-----------------|
| Composition 1                                                                       | A               |
| Composition 7                                                                       | A               |
| Composition A                                                                       | A               |
| Composition 6                                                                       | A               |
| Composition xx (acid-treated gas oil containing 5% peanut oil)                      | E               |
| Composition YY (acid-treated gas oil containing 1% 2,4-ditertbutyl-6-methyl phenol) | D               |
| Composition ZZ (acid-treated gas oil containing 10% tetralin)                       | D               |
| Non-acid-treated gas oil                                                            | E               |
| Acid-treated gas oil                                                                | C               |

In conjunction with compositions of this in-

vention minor amounts of generally less than 1% of other additives can be added, if desired, in order to fortify the compositions:

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          | Ravison            |
| Seed            | Sesame             |
| Olive           | Sunflower          |
| Kernel palm oil | Teaseed oils, etc. |

3. Marine oils—

|                                |
|--------------------------------|
| Codfish                        |
| Codliver                       |
| Dogfish                        |
| Dolphin body                   |
| Dolphin fish                   |
| Herring                        |
| Japfish                        |
| Menhaden oils                  |
| Porpoise body and jaw oils     |
| Salmon oil                     |
| Sardine and sardine liver oils |
| Seal oil                       |
| Shark and shark liver oils     |
| Sperm whale body and head oils |
| Whale oil, etc.                |

B. Naturally occurring fatty acids of high molecular weights:

1. Saturated—

|           |                      |
|-----------|----------------------|
| Capric    | Stearic              |
| Undecylic | Arachidic            |
| Lauric    | Lignoceric           |
| Myristic  | Cerolic              |
| Palmitic  | Montanic acids, etc. |

B. Naturally occurring fatty acids of high molecular weights:—Continued

2. Unsaturated—

|          |           |
|----------|-----------|
| Oleic    | Linoleic  |
| Linoleic | Brassidic |
| Erucic   | Elaidic   |

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 monooleate, methyl dichlorostearate, diglycol stearate di-2-ethyl hexyl-azelate diglycol laurate, n-decyl hydrogen phthalate or succinate, octadecyl stearate, polyalkylene glycol esters of monocarboxylic acids.

2. Esters of inorganic acids, e. g. tricresyl phosphate and 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

E. Halogen-containing materials, e. g.:

Chlorinated paraffin waxes

Chlorinated paraffin fatty acids and esters

Chlorinated aromatic compounds

Chlorinated organic compounds containing sulfur

F. Natural occurring and synthetic waxes

Montan wax

Carnauba wax

Beeswax

Spermaceti

Castor oil distillate

Ozokerite, etc.

Polyalkylene glycol polymers, e. g.

Polyethylene glycol and the like.

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, dipping, or the like. It may be applied on the sheet metal prior to, during or after rolling. Preferably the lubricant is warmed to about a temperature of 150 to 175° F. before applying it to the rolls so as to aid in spreading the lubricant more evenly on the rolls and work piece.

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 require 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.

I claim as my invention:

1. A metal working lubricant comprising a sulfuric acid-treated light liquid hydrocarbon having a boiling range of from 300° F. to about 700° F. having incorporated therein from 3 to 10% of a

fatty material selected from the class consisting of lanolin, oleyl alcohol and olein.

2. A metal working lubricant comprising a sulfuric acid-treated light liquid hydrocarbon having a boiling range of from 300° F. to about 700° F. having incorporated therein from 3 to 10% of lanolin.

3. A metal working lubricant comprising a sulfuric acid-treated liquid hydrocarbon having a boiling range of from 300° F. to about 700° F. having incorporated therein from 3 to 10% of oleyl alcohol.

4. A metal working lubricant comprising a sulfuric acid-treated light liquid hydrocarbon having a boiling range of from 300° F. to about 700° F. having incorporated therein from 3 to 10% of olein.

5. A metal working lubricant consisting essentially of a major amount of gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of gas oil from 3 to 10% of a fatty material selected from the class consisting of lanolin, oleyl alcohol, and olein.

6. A metal working lubricant consisting essentially of a major amount of an oxidized gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of gas oil and from 3 to 10% of a fatty material selected from the class consisting of lanolin, olein and oleyl alcohol.

7. A metal working lubricant comprising gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of oil and having incorporated therein from 3 to 10% of lanolin.

8. A metal working lubricant comprising gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of oil and having incorporated therein from 3 to 10% of oleyl alcohol.

9. A metal working lubricant comprising gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of oil and having incorporated therein from 3 to 10% of olein.

10. A metal working lubricant comprising an oxidized gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of oil and having incorporated therein from 3 to 10% of lanolin.

11. A metal working lubricant comprising an oxidized gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of oil and having incorporated therein from 3 to 10% of oleyl alcohol.

12. A metal working lubricant comprising an oxidized gas oil which has been acid treated with from 6 to 20 pounds of 87-95% sulfuric acid per barrel of oil and having incorporated therein from 3 to 10% of olein.

13. A metal working lubricant consisting essentially of a major amount of a gas oil which has been acid treated with about 20 pounds of 93% sulfuric acid per barrel of gas oil and from 3 to 10% of a fatty material selected from the class consisting of lanolin, oleyl alcohol and olein and from 0.01 to 1% of an oil-soluble polyalkyl phenol.

14. A metal working lubricant consisting essentially of a major amount of a gas oil which has been acid treated with about 20 pounds of 93% sulfuric acid per barrel of gas oil and from 3 to 10% of a fatty material selected from the class consisting of lanolin, oleyl alcohol and olein, and 0.01 to 1% of a metal naphthenate.

9

15. A metal working lubricant comprising the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Lanolin                                          | 4-6      |
| Acid-treated gas oil in accordance with claim 13 | 96-94    |

16. A metal working lubricant comprising the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Oleyl alcohol                                    | 4-6      |
| Acid-treated gas oil in accordance with claim 13 | 96-94    |

17. A metal working lubricant comprising the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Olein                                            | 4-6      |
| Acid-treated gas oil in accordance with claim 13 | 96-94    |

18. A metal working lubricant consisting essentially of the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Lanolin                                          | 3-6      |
| Ca naphthenate                                   | 0.6-0.8  |
| Acid treated gas oil in accordance with claim 13 | Balance  |

19. A metal working lubricant consisting essentially of the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Oleyl alcohol                                    | 3-6      |
| Ca naphthenate                                   | 0.6-0.8  |
| Acid treated gas oil in accordance with claim 13 | Balance  |

20. A metal working lubricant consisting essentially of the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Lanolin                                          | 3-6      |
| 2,4 ditertbutyl-6-methylphenol                   | 0.6-0.8  |
| Acid treated gas oil in accordance with claim 13 | Balance  |

10

21. A metal working lubricant consisting essentially of the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Oleyl alcohol                                    | 3-6      |
| 2,4 ditertbutyl-6-methylphenol                   | 0.6-0.8  |
| Acid treated gas oil in accordance with claim 13 | Balance  |

22. A metal working lubricant consisting essentially of the following ingredients in the following proportions:

|                                                  | Per cent |
|--------------------------------------------------|----------|
| Lanolin                                          | 3-6      |
| Diphenylamine                                    | 0.6-0.8  |
| Acid treated gas oil in accordance with claim 13 | Balance  |

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