

[54] **WORKING OF NON-FERROUS METALS**
[75] Inventor: **Edwin J. Latos**, Chicago, Ill.
[73] Assignee: **Universal Oil Products Company**,
Des Plaines, Ill.
[22] Filed: **May 12, 1972**
[21] Appl. No.: **252,798**

[52] **U.S. Cl.**..... **184/1 E, 72/42, 252/50**
[51] **Int. Cl.**..... **F01m 1/00**
[58] **Field of Search**..... **252/50; 72/42; 184/1 E**

[56] **References Cited**
UNITED STATES PATENTS
3,216,939 11/1965 Cyba..... 252/50

3,347,791 10/1967 Thompson et al. 252/50
3,372,112 5/1968 Parker 252/50

Primary Examiner—Patrick P. Garvin
Assistant Examiner—Andrew H. Metz
Attorney, Agent, or Firm—James R. Hoatson, Jr.; Ber-
nard L. Kramer; William H. Page, II

[57] **ABSTRACT**
In the working of non-ferrous metals, particularly zir-
conium or alloy thereof or titanium or alloy thereof,
the improved method of using a mono- or polyamine
containing at least 12 carbon atoms as a lubricant.

9 Claims, No Drawings

WORKING OF NON-FERROUS METALS

BACKGROUND OF THE INVENTION

In the working of metal, wherein two metal surfaces are in movable contact with each other, a lubricant is needed to serve as an antiwear and antiseize agent, as well as a coolant. The requirements for a lubricant in the working of non-ferrous metals is considerably more severe than in the working of ferrous metals and particularly zirconium or alloy thereof or titanium or alloy thereof.

DESCRIPTION OF THE INVENTION

In addition to serving as an antiwear and antiseize agent, as well as a coolant, the lubricant must survive the chemical and thermal environment at the interface to avoid formation of debris which is difficult to remove from the finished article. The lubricant further must avoid corrosion of the metal, staining and excessive altering of the surface structure of the metal. This latter requirement is particularly important in the case of zirconium and titanium because of the desirability to prevent formation of the open grain surface.

In accordance with the present invention, lubrication of the non-ferrous metal is accomplished by utilizing a lubricant comprising a mono- or polyamine containing at least 12 carbon atoms.

While the present invention is particularly applicable to the working of zirconium or alloy thereof and titanium or alloy thereof, it is understood that it also may be used to advantage in the working of other non-ferrous metals including, for example, aluminum, copper, brass, bronze, magnesium, etc. The working of the metal may take various forms including drawing, rolling, extruding, cutting, drilling, broaching, tapping, threading, swaging, tube reducing, etc.

In a preferred embodiment, the lubricant is a N,N'-di-substituted-diaminodiphenylalkane. Of particular advantage are the 4,4'-di-(secalkylamino)-diphenylpropanes in which each alkyl contains from 3 to 20 carbon atoms or more. Illustrative compounds in this embodiment include 4,4'-di-(isopropylamino)-diphenylpropane, 4,4'-di-(secbutylamino)-diphenylpropane, 4,4'-di-(secpentylamino)-diphenylpropane, 4,4'-di-(sechexylamino)-diphenylpropane, 4,4'-di-(secheptylamino)-diphenylpropane, 4,4'-di-(secoctylamino)-diphenylpropane, 4,4'-di-(secnonylamino)-diphenylpropane, 4,4'-di-(secdecylamino)-diphenylpropane, 4,4'-di-(secundecylamino)-diphenylpropane, 4,4'-di-(secdodecylamino)-diphenylpropane, 4,4'-di-(sectridcylamino)-diphenylpropane, 4,4'-di-(sectetradecylamino)-diphenylpropane, 4,4'-di-(secpentadecylamino)-diphenylpropane, 4,4'-di-(sechexadecylamino)-diphenylpropane, 4,4'-di-(secheptadecylamino)-diphenylpropane, 4,4'-di-(secoctadecylamino)-diphenylpropane, 4,4'-di-(secnonadecylamino)-diphenylpropane, 4,4'-di-(seceicosylamino)-diphenylpropane, etc. While the secalkyl configuration is preferred, it is understood that the corresponding primary or tertiary alkyl substituted compounds also are comprised within the scope of the present invention.

In another embodiment, the N,N'-di-substituted amino-diphenylpropanes comprise N,N'-di-(cycloalkylamino)-diphenylpropanes in which the cycloalkyl

contains from 3 to 12 and more particularly 5 to 8 carbon atoms in the ring. A particularly preferred compound of this embodiment is 4,4'-di-(cyclohexylamino)-diphenylpropane. Other compounds in this embodiment include 4,4'-di-(cyclobutylamino)-diphenylpropane, 4,4'-di-(cyclopentylamino)-diphenylpropane, 4,4'-di-(cycloheptylamino)-diphenylpropane, 4,4'-di-(cyclooctylamino)-diphenylpropane, etc.

While the 4,4'-di-(substituted amino)-diphenylpropanes are preferred, it is understood that the corresponding 2,2'-, 2,3'-, 2,4'-, 3,3'- and 3,4'- substituted compounds also are comprised within the scope of the present invention. One or both of the phenyl rings may contain substituents attached thereto, which substituents may comprise alkyl or dialkyl of from 1 to about 10 carbon atoms each, halogen, including chlorine, bromine, iodine or fluorine, sulfur as mercapto or thioether, alkylamino or dialkylamino in which the alkyl contains from 1 to about 10 carbon atoms each, etc. It is understood that one or both of the phenyl rings may be substituted with one or two of the substituents set forth above. In a preferred embodiment, the substitutions are not in a position ortho to the nitrogen atoms. It is understood that the variously substituted compounds are not necessarily equivalent.

While the di-substituted-diamino-diphenylpropanes are preferred, it is understood that the correspondingly substituted diaminodiphenylalkanes in which the alkane moiety contains from 1 to 8 and more particularly from 1 to 6 carbon atoms are contemplated for use in the present invention. These comprise the correspondingly substituted diamino-diphenylmethanes, ethanes, butanes, pentanes, hexanes, etc.

In another embodiment, the lubricant comprises an alkylamine containing at least 12 carbon atoms and more specifically from 12 to about 40 carbon atoms per molecule. Illustrative amines in this embodiment include dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, nonadecylamine, eicosylamine, heneicosylamine, docosylamine, tricosylamine, tetracosylamine, pentacosylamine, hexacosylamine, heptacosylamine, octacosylamine, nonacosylamine, triacontylamine, hentriacontylamine, dotriacontylamine, tritriacontylamine, tetratriacontylamine, pentatriacontylamine, hexatriacontylamine, heptatriacontylamine, octatriacontylamine, nonatriacontylamine, tetracontylamine, etc. Conveniently, the amine is derived from fatty acids which may comprise one or more of lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, palmitoleic acid, maleic acid, ricinoleic acid, petroselinic acid, vaccenic acid, linoleic acid, linolenic acid, eleostearic acid, licanic acid, parinaric acid, gadoleic acid, arachidonic acid, cetoleic acid, erucic acid, selacholeic acid, etc., or mixtures as tallow amine, coconut amine, etc., as well as the hydrogenated products thereof.

In still another embodiment, the lubricant comprises a dialkylamine in which the total number of carbon atoms is at least 12 and more specifically from 12 to about 40 carbon atoms. Illustrative amines in this embodiment include dihexylamine, diheptylamine, dioctylamine, dinonylamine, didodecylamine, diundecylamine, didodecylamine, ditridecylamine, ditetradecylamine, dipentadecylamine, dihexadecylamine, diheptadecylamine, dioctadecylamine, dinonadecylamine,

dieicosylamine, etc. Here again, the amine is conveniently derived from fatty acids and will be selected from those specifically set forth in the preceding paragraph.

In another embodiment, the lubricant is a polyamine containing at least 12 carbon atoms. In one embodiment, the polyamine is a N-alkyl, N,N-dialkyl or N,N'-dialkyldiaminoalkane in which the alkyl contains from 3 to about 30 carbon atoms each and the alkane moiety contains from 2 to about 6 carbon atoms, with the understanding that the total number of carbon atoms is at least 12. In the N-alkyl derivatives, the alkyl contains from 6 to 30 carbon atoms but again with the understanding that the total number of carbon atoms in the molecule is at least 12. Preferred compounds in this embodiment include N-alkyl-1,3-diaminopropanes including N-nonyl-1,3-diaminopropane, N-decyl-1,3-diaminopropane, N-undecyl-1,3-diaminopropane, N-dodecyl-1,3-diaminopropane, N-tridecyl-1,3-diaminopropane, N-tetradecyl-1,3-diaminopropane, N-pentadecyl-1,3-diaminopropane, N-hexadecyl-1,3-diaminopropane, N-heptadecyl-1,3-diaminopropane, N-octadecyl-1,3-diaminopropane, N-nonadecyl-1,3-diaminopropane, N-eicosyl-1,3-diaminopropane, etc., N,N-dipentyl-1,3-diaminopropane, N,N-dihexyl-1,3-diaminopropane, N,N-diheptyl-1,3-diaminopropane, N,N-dioctyl-1,3-diaminopropane, N,N-dinonyl-1,3-diaminopropane, N,N-didecyl-1,3-diaminopropane, N,N-diundecyl-1,3-diaminopropane, N,N-didodecyl-1,3-diaminopropane, N,N-ditridecyl-1,3-diaminopropane, N,N-ditetradecyl-1,3-diaminopropane, N,N-dipentadecyl-1,3-diaminopropane, N,N-dihexadecyl-1,3-diaminopropane, etc., N-methyl-N-octyl-1,3-diaminopropane, N-methyl-N-nonyl-1,3-diaminopropane, N-methyl-N-decyl-1,3-diaminopropane, N-methyl-N-undecyl-1,3-diaminopropane, N-methyl-N-dodecyl-1,3-diaminopropane, N-methyl-N-tridecyl-1,3-diaminopropane, N-methyl-N-tetradecyl-1,3-diaminopropane, N-methyl-N-pentadecyl-1,3-diaminopropane, N-methyl-N-hexadecyl-1,3-diaminopropane, etc., N-ethyl-N-heptyl-1,3-diaminopropane, N-ethyl-N-octyl-1,3-diaminopropane, N-ethyl-N-nonyl-1,3-diaminopropane, N-ethyl-N-decyl-1,3-diaminopropane, N-ethyl-N-undecyl-1,3-diaminopropane, N-ethyl-N-dodecyl-1,3-diaminopropane, etc., N-propyl-N-hexyl-1,3-diaminopropane, N-propyl-N-heptyl-1,3-diaminopropane, N-propyl-N-octyl-1,3-diaminopropane, N-propyl-N-nonyl-1,3-diaminopropane, N-propyl-N-decyl-1,3-diaminopropane, N-propyl-N-undecyl-1,3-diaminopropane, N-propyl-N-dodecyl-1,3-diaminopropane, etc., N-butyl-N-pentyl-1,3-diaminopropane, N-butyl-N-hexyl-1,3-diaminopropane, N-butyl-N-heptyl-1,3-diaminopropane, N-butyl-N-octyl-1,3-diaminopropane, N-butyl-N-nonyl-1,3-diaminopropane, N-butyl-N-decyl-1,3-diaminopropane, N-butyl-N-undecyl-1,3-diaminopropane, N-butyl-N-dodecyl-1,3-diaminopropane, etc., N,N'-dipentyl-1,3-diaminopropane, N,N'-dihexyl-1,3-diaminopropane, N,N'-diheptyl-1,3-diaminopropane, N,N'-dioctyl-1,3-diaminopropane, N,N'-dinonyl-1,3-diaminopropane,

N,N'-didecyl-1,3-diaminopropane, N,N'-diundecyl-1,3-diaminopropane, N,N'-didodecyl-1,3-diaminopropane, N,N'-ditridecyl-1,3-diaminopropane, N,N'-ditetradecyl-1,3-diaminopropane, N,N'-dipentadecyl-1,3-diaminopropane, N,N'-dihexadecyl-1,3-diaminopropane, etc., correspondingly substituted 1,2-diaminoethanes, 1,2-diaminopropanes, 1,2-diaminobutanes, 1,3-diaminobutanes, 1,4-diaminobutanes, 1,2-diaminopentanes, 1,3-diaminopentanes, 1,4-diaminopentanes, 1,5-diaminopentanes, 1,2-diaminohexanes, 1,3-diaminohexanes, 1,4-diaminohexanes, 1,5-diaminohexanes, 1,6-diaminohexanes, etc. Other illustrative polyamines include similarly substituted dialkylene triamines, trialkylene tetramines, tetraalkylene pentamines, pentaalkylene hexamines, etc., and these compounds in which one or more of the additional nitrogen atoms also contain alkyl substitutions. It is understood that a mixture of the polyamines may be used and that the different amine compounds are not necessarily equivalent.

In one embodiment, the amine compound is utilized neat as the lubricant. In another embodiment, the amine compound may be used in admixture with other lubricating ingredients and may be in the form of a solution or emulsion. The lubricating composition may contain mineral oil, sulfonated oil, alcohol, ether, fatty acid, fatty acid ester, alkanolamine soap of fatty acid, alkali metal soap of fatty acid, salts, organic nitrates, inorganic nitrates, various water based lubricants, etc. When the additional ingredient does not form a solution with the amine compound, the composition may be utilized as an emulsion, either with or without water. In general, these additional ingredients will be selected from those described in the prior art. The amine may be used in these compositions in the range of from about 1 percent to about 99 percent and preferably from about 2 percent to about 50 percent by weight of the final composition, exclusive of water or solvent used in the final composition.

The lubricant of the present invention is utilized in conventional manner, which will depend on the particular procedure employed in the working of the metal. In any event, the lubricant must be applied in a manner that it will be present at the points of contact of the metals in moving relationship to each other. Also, the amount of lubricant will be sufficient to accomplish effective lubrication, which amount also will depend upon the particular working procedure employed.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

The lubricants were evaluated in a modified Bowden-Leben pin and disc machine. The Bowden-Leben method is described in "The Friction and Lubrication of Solids," 1954, page 74, by Bowden and Tabor. This method is also discussed in the article by E. Rabinowicz, entitled "The Boundary Friction of Very Well Lubricated Surfaces," which was presented at the A.S.L.E. Ninth Annual Meeting in Cincinnati on April 5, 1954, and published in the July-August 1954 issue of "Lubricating Engineering." In the modification used for the runs reported herein, a polished A-8 steel disc rotates in contact with an upwardly extended rounded

Zircaloy pin. Zircaloy No. 2, for example, is an alloy comprising 98.3 percent by weight zirconium, 1.5 percent by weight tin, 0.2 percent by weight iron and 0.1 percent by weight chromium.

A total of about 2 g. of lubricant is utilized. About 1.8 g. of lubricant is applied to the disc and about 0.2 g. of lubricant is applied to the pin. The equipment is enclosed in a housing which is heated for varying the temperature of the run which, in these evaluations, can be within the range of from 72° to 212°F. The speed is fixed at 6 rpm. In each run an original load of 100 g. is increased in units of 100 g. at intervals of 1.67 minutes to a maximum load of 1,300 g. A strain gage circuit is used as sensing element in converting the frictional effects into equivalent electrical responses, which then are recorded on a continuous chart recorder. The coefficient of friction is determined for each time interval. In addition, the diameter of the wear spot on the pin is measured. The pin and disc are visually inspected immediately after the test to determine the amount of debris.

The following table reports results which were obtained in the above manner when using 4,4'-di-(sec-butylamino)-diphenylpropane as the lubricant. Two separate runs were made, one at 72°F. and the other at 210°F. The coefficient of friction at the various time intervals, the wear area and the amount of debris are reported in the following table.

TABLE I

Load, g.	Time, min.	Temperature	
		72°F.	210°F.
100	1.67	0.117	0.125
200	3.34	0.108	0.125
300	5.01	0.103	0.125
400	6.68	0.104	0.125
500	8.35	0.105	0.127
600	10.02	0.102	0.127
700	11.69	0.103	0.131
800	13.36	0.101	0.138
900	15.03	0.101	0.138
1000	16.70	0.103	0.139
1100	18.37	0.104	0.138
1200	20.04	0.103	0.141
1300	22.00	0.103	0.145
1300	37.00	0.102	0.143
1300	52.00	0.103	0.127
1300	67.00	0.103	0.118
1300	82.00	0.101	0.114
1300	97.00	0.103	0.113
1300	112.00	0.103	0.103
1300	127.00	0.103	0.098
1300	142.00	0.103	0.094
1300	157.00	0.100	0.092
1300	172.00	0.100	0.095
1300	187.00	0.100	0.095
1300	202.00	0.099	0.097
Wear Area, mm ²		0.045	0.126
Debris		Very	Light
		Light	

From the data in the above table, it will be noted that the coefficient of friction was satisfactory in both runs. It is especially noteworthy that the wear was very low and the amount of debris was very small.

EXAMPLE II

This example illustrates the use of hydrogenated tallow amine as a lubricant, which was evaluated in the same manner as described in Example I. This amine is

available commercially as "Armeen HTD." The run was made at 210°F. The coefficient of friction initially was 0.084 and at a final load of 1,300 g. after 202 minutes, the coefficient of friction was 0.042. The amount of debris was light, and the wear area was 0.113 mm².

EXAMPLE III

Example II is an illustration using an alkyl primary amine. This example illustrates the use of a secondary alkyl amine. The amine used in this example is di(hydrogenated tallow)-amine and is available commercially as "Armeen 2 HT." The evaluation was made in the same manner as described in Example I at a temperature of 210°F. The coefficient of friction ranged from the initial of 0.092 to 0.043 at a final load of 1,300 g. after 202 minutes. The amount of debris was light and the wear area was 0.113 mm².

EXAMPLE IV

This example illustrates the use of a diamine as the lubricant and was evaluated in the same manner as described in Example I at a temperature of 210°F. The diamine used in this run is N-tallow-1,3-diaminopropane and is available commercially as "Duomeen T." The coefficient of friction ranged from an initial of 0.100 to 0.062 at a load of 1300 g. after 202 minutes. The amount of debris was light and the wear area was 0.283 mm².

EXAMPLE V

As hereinbefore set forth, the amine may be used in a mixture with other ingredients. In this example, a mixture of 10 percent by weight of 4,4'-di-(sec-butylamino)-diphenylpropane and 90 percent by weight of refined mineral oil was utilized as the lubricant and evaluated in the same manner as described in Example I at a temperature of 72°F. The mineral oil is available commercially as "Sentry 20" and is a solvent extracted neutral oil having a viscosity, SUS, of 205 at 100°F. The coefficient of friction in this run decreased from 0.108 to 0.095 after 202 minutes at a final load of 1,300 g. The wear area was 0.113 mm² and the amount of debris was moderate to heavy.

I claim as my invention:

1. In the working of non-ferrous metal selected from the group consisting of zirconium, zirconium alloys, titanium and titanium alloys, wherein said non-ferrous metal is in contact with another metal, the method which comprises applying, as a lubricant, to the points of contact of said metals in moving relationship to each other, a hydrocarbyl mono- or polyamine containing at least 12 carbon atoms.

2. The method of claim 1 in which said amine is a N, N'-di-substituted-diaminodiphenylalkane in which the alkane moiety contains from 1 to 8 carbon atoms.

3. The method of claim 2 in which said amine is a 4,4'-di-(secalkylamino)-diphenylpropane in which each alkyl contains from 3 to 20 carbon atoms.

4. The method of claim 2 in which said amine is 4,4'-di-(cycloalkylamino)-diphenylpropane in which the cycloalkyl contains from 3 to 12 carbon atoms in the ring.

5. The method of claim 1 in which said amine is an alkyl primary amine in which the alkyl contains from 12 to 40 carbon atoms.

7

6. The method of claim 1 in which said amine is a dialkylamine in which each alkyl contains from 6 to 40 carbon atoms.

7. The method of claim 6 in which said amine is dital-low amine.

8. The method of claim 1 in which said amine is a N-alkyldiaminoalkane in which the alkyl contains from 6

8

to 30 carbon atoms and the alkane moiety contains from 2 to 6 carbon atoms, with the total number of carbon atoms being at least 12.

5 9. The method of claim 8 in which said amine is N-tallow-1,3-diaminopropane.

* * * * *

10

15

20

25

30

35

40

45

50

55

60

65