

1

2,960,466

**HALOGENATED HYDROCARBON LUBRICANTS
CONTAINING HEAT TREATED BORON NITRIDE**

Charles E. Saunders, Silver Spring, Md., assignor to the
United States of America as represented by the Secretary of the Navy

No Drawing. Filed June 13, 1956, Ser. No. 591,254

1 Claim. (Cl. 252—25)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to halogenated hydrocarbon lubricants and more particularly to additives for increasing the lubricating qualities of such lubricants.

This application is a continuation-in-part of my co-pending application Serial No. 213,037, filed February 27, 1951, now abandoned.

Many halogenated hydrocarbons, i.e. hydrocarbons wherein fluorine or chlorine atoms are attached to the carbon atoms of the hydrocarbon skeleton structure, have been prepared and have been found to have good lubricating qualities. Of particular interest are the fluorocarbons which have been found to have high resistance to both thermal decomposition and chemical reaction. Their high resistance to chemical action, complete lack of toxicity, resistance to thermal decomposition and the fact that when they do decompose no toxic products issue therefrom make the use of fluorocarbon lubricants highly desirable for specialized applications. Air compressors, for example, now need to be carefully designed so as to prevent explosions due to combustion of the conventional petroleum oils used as lubricants. When fluorocarbon lubricants are utilized in these compressors not only is the fire hazard reduced because of the low combustibility of the lubricants but because of the resistance of these lubricants to oxidation the compressors may be used in the presence of such highly oxidized gases as oxygen and chlorine. Of particular interest in this regard is the development of a lubricant suitable for use in equipment utilizing high strength hydrogen peroxide. The primary interest at present is in the development of a peroxide pump lubricant. The violent oxidation characteristics of hydrogen peroxide eliminate the possibility of using conventional petroleum lubricants and most of the available synthetic lubricants. Of the commercially available lubricants only the fluorocarbons were found to be compatible with hydrogen peroxide. However the halogenated hydrocarbon lubricants and particularly the fluorocarbons while possessing the aforementioned desirable characteristics have lubricity characteristics which do not compare favorably with the lubricity characteristics of the highly developed petroleum lubricants.

Attempts have therefore been made to improve the lubricity characteristics of the fluorocarbons and the other halogenated hydrocarbons by the incorporation of suitable additives. Conventional petroleum oil additives were found to be unsuitable either because the additives were not compatible with strong oxidizing agents such as hydrogen peroxide or because stable suspensions of the additives in the halogenated hydrocarbon lubricants could not be obtained without great difficulty.

It is, therefore, an object of the present invention to provide an additive for halogenated hydrocarbon lubri-

2

cants which greatly increases their lubricity and anti-wear characteristics.

Another object is to provide an additive for halogenated hydrocarbon lubricants which is compatible with strong oxidizing agents.

A further object is to provide a method of producing an improved additive for increasing the lubricity characteristics of halogenated hydrocarbon lubricants.

A still further object is to provide a method of preparing improved halogenated hydrocarbon lubricants.

Other objects and the attendant advantages of the invention will become apparent to those skilled in the art as the invention is disclosed in the following detailed description.

The foregoing objects and the attendant advantages of the invention may be accomplished through the addition of a small quantity of heat treated boron nitride to the halogenated hydrocarbon lubricant. It has been found that heat treated boron nitride is easily dispersed in these lubricants and that the addition of a small quantity in the order of 0.75% will increase the lubricity of the lubricants to a marked degree.

Boron nitride if prepared at a low temperature appears as a colorless amorphous gelatine which dries to a hard brittle mass. In this state the boron nitride provides some improved lubricity to the halogenated hydrocarbon lubricants but is chemically reactive. However, I have found that if the amorphous boron nitride is first heated to a high temperature, i.e. about red heat, and allowed to cool slowly its capability of increasing the lubricity of the halogenated hydrocarbon lubricants is greatly increased. Upon being heated to red heat, at about 2500° C., the boron nitride takes on a dark color and appears to assume a more rigid crystalline structure which is practically insensitive to chemical action. This heat treated boron nitride was found to disperse easily in the fluorocarbon lubricants and to be greatly superior to other suggested additives such as Molykote (molybdenum disulfide), graphite or Liqui-Moly (molybdenum disulfide plus a solvent) in improving the lubricating qualities of the aforementioned lubricants.

Wear tests have been made of the fluorocarbon lubricants which were found to be impact insensitive with hydrogen peroxide. Those lubricants found best for the purpose are the Fluorolube oils which are partially fluorinated hydrocarbons obtained from the Hooker Electrochemical Company. The Fluorolubes are described by the manufacturer in Hooker Bulletin Nos. 15 and 30 as addition polymers of trifluorovinyl chloride built up of a recurring unit which is $(-CF_2-CFCl-)$. They vary from low viscosity colorless oils through heavy oils to opaque grease-like materials. They are complex mixtures and not single chemical species. The various grades are obtained through the distillation of the basic polymer and vary in density from approximately 1.88 gm./cc. at 25° C. for the lighter oils to approximately 2.0 gm./cc. for the heavy greases. Fluorolube S and Fluorolube FS are preferred for use with strong oxidizing agents. At normal temperatures these fluorocarbons are water-white, colorless, mobile liquids. Fluorolube FS has a melting point of -60° C. and a density at 100° F. of 1.86 gm./cc., viscosity 5 centistokes. Fluorolube S has a melting point of -15° C. and a density at 100° F. of 1.93 gm./cc., viscosity 100 centistokes similar in viscosity to SAE 30 oil. Other lubricants, such as the Kel-Flo polymer oils which are lubricants similar to Fluorolubes manufactured by the M. W. Kellogg Co. and Perfluorolube oils which are completely fluorinated hydrocarbons manufactured by the E. I. du Pont de Nemours Corp., may also be used if desired.

The testing machine used to evaluate these oils was a constant speed (1800 r.p.m.) electric motor with a hardened steel wheel attached to the shaft. The wheel was 1½ in. in diameter and had a radius of thickness of ⅛ in. on the working surface. This wheel was hardened to Rockwell 58c. The motor was attached to a base plate which also holds a lever arrangement that permits loading of the test piece. The test pieces are cold rolled steel ½" x 2" x ⅜". The loading was accomplished by using the lever arrangement to force the test piece against the wheel. A 5:1 lever ratio gave a 20 pound loading at the point of contact. The tested lubricant was fed from a drip oiler so the oil just contacted the edge of the wheel as it was fed. The samples and test wheel were finished with No. LN3 crocus cloth and cleaned prior to each run. The test was started by allowing the oil to completely cover the sample and to flow at a certain arbitrary drip rate (90 drops per min.) which was maintained for the duration of the run. The test was started by allowing the sample to come into contact with the wheel at a controlled rate. At the instant the wheel and sample came into contact the time measurement was started and the test allowed to run for 5 minutes. The test was secured by removing the sample from contact with the wheel and turning off the motor. If during the run the drip oiler ran low on oil the oiler was refilled as often as necessary to enable the test to run to completion. The resultant length of mark on the test sample served as a comparative measurement of the quality of the lubricant tested.

Boron nitride which will pass through a 325 mesh screen may be suspended in the Fluorolube oils without difficulty. In this the boron nitride is superior to graphite and molybdenum disulfide because these additives require the addition of oleic acid as a dispersion agent before they can be suspended in the lubricant. The boron nitride requires only a slight agitation to achieve suspension in Fluorolube S. Oleic acid may also be added to the boron nitride to assist in achieving a suspension in Fluorolube FS and other halogenated hydrocarbon lubricants.

To render the boron nitride hard and insensitive to chemical action and to increase the lubricating characteristics in accordance with this invention the boron nitride must be heated to a temperature near but below the melting point. The boron nitride may be heated in a crucible by a blast gas-flame to approximately 2500° C. When so heated the boron nitride darkens and hardens without igniting or burning. The boron nitride is maintained at the high temperature until the whole mass assumes the dark coloration. Ten minutes has been found sufficient time for small quantities. This treatment results in the transformation of the white, gray or colorless amorphous boron nitride into a hard, dark, material having a six-sided tabular crystalline structure. The heat treated boron nitride is chemically inert not being attacked by acids or alkali at high temperatures and is not ignited when heated to high temperatures in an atmosphere of hydrogen. As little as 0.50% by weight of this heat treated boron nitride greatly increases the lubricity characteristics of halogenated hydrocarbon lubricants such as the fluorocarbons.

Table I shows the results obtained by the above described wear test as applied to petroleum oils, Fluorolube oils and Fluorolube oils with a small part by weight of heat treated boron nitride added thereto for comparison.

Table I

Lubricant Composition	Wear Mark in In.	
	Test I	Test II
Petroleum Oil SAE 10.....	0.123	0.131
Petroleum Oil SAE 50.....	0.141	0.135
Fluorolube S.....	0.130	0.128
Fluorolube S+0.75% BN.....	0.056	0.062
Fluorolube FS.....	0.169	0.174
Fluorolube FS+0.75% BN.....	0.139	0.135

From the test results given in Table I it may be seen that the addition of a small percentage by weight of the heat treated boron nitride to the Fluorolube oils reduced the wear mark by as much as 42%.

From the foregoing detailed description it may be seen that there has been provided an additive which greatly increases the lubricating qualities of the halogenated hydrocarbon lubricants and which is chemically inert and resists oxidation in the presence of strong oxidizing agents at high temperatures. This additive makes possible the use of the fluorocarbon lubricants and other halogenated hydrocarbon lubricants in the presence of strong oxidizing agents such as concentrated acids, hydrogen peroxide, ozone, etc. as may be encountered in the propulsion units of torpedoes, submarines, rockets, guided missiles and the like with greatly improved results.

The present invention is not to be considered as limited by any of the examples described herein which are given by way of illustration only, but is to be limited solely by the terms of the appended claim.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

The method of improving the lubricity characteristics of a halogenated hydrocarbon lubricant which comprises; heating boron nitride to a red heat, slowly cooling the boron nitride, adding to the lubricant from about 0.5 to about 0.75 percent by weight of said boron nitride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,156,803	Cooper	May 2, 1939
2,411,159	Hanford	Nov. 19, 1946
2,467,145	Morway et al.	Apr. 12, 1949
2,551,639	Feasley et al.	May 8, 1951
2,628,196	Coonrad et al.	Feb. 10, 1953

FOREIGN PATENTS

12,377	Great Britain	of 1913
--------	---------------------	---------

OTHER REFERENCES

"The Fluorocarbons," Chemical Engineering, July 1950, pages 129-136.

Boron Nitride—An Unusual Refractory, Amer. Ceramic Soc. Bulletin, vol 31, #4 (1952).