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LUBRICANT FOR HIGH BEARING PRESSURES

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The present invention relates to improved lubricants especially leaded lubricants of the type adapted to withstand extremely high bearing pressures. The invention will be fully understood from the following description.

During the last several years the need for efficient lubricants adapted to withstand extreme bearing pressures has become more acute and among the various types proposed the leaded compounds have found a definite place, especially for use in automotive transmissions or other power transmitting devices where steel bearing members are in contact under high pressures of the order of 300,000 pounds per square inch or higher.

Leaded compounds had been previously proposed and it has been found desirable to include sulfur-containing materials in these compositions but there has been little uniformity among the compositions produced and great variation in the quality of the products. This has been due not only to the different forms in which the lead is present, but also to the different base stocks, some of which contained sulfur in different proportions. While it has been the general opinion that sulfur is desirable in such compositions, there was little exact knowledge as to the reason therefor and its actual effect.

It has now been found that all sulfur compounds are not equally effective, in fact some sulfur compounds are of no value whatever others are better, for example, satisfactory at low speeds, but that to exploit the full capabilities of the leaded compounds the sulfur must not only be of a particular type but likewise the lead and sulfur must be in particular relative proportions. In this manner extremely valuable products are obtained which are capable of carrying the highest required loads under high speeds now necessary for automotive equipment, especially hypoid gears.

The present investigation of leaded sulfur compounds has brought out the fact that to be most effective the sulfur present must be in a reactive form. In the following description the type of sulfur compound has been described generally as "corrosive." This does not mean that it has objectionable properties when stored in metal containers or on machine parts and the like, but the term is used to designate the various types of sulfur compounds which will discolor a bright copper strip when in contact therewith.

As indicated above, it is also necessary that there be sufficient "corrosive" sulfur to carry the load and lead be sufficient in amount to form lead sulphide (PbS). It should be repeated that the total sulfur is in no case to be considered here but only that proportion of the sulfur which is of the corrosive type. The amount of corrosive sulfur present should ordinarily be above .2% and generally from .3 to 1.5% of the total composition for most purposes and the amount of lead would be sufficient to form lead sulphide with the corrosive sulfur present. For economy, it is preferred not to have an excess of lead, but if present it is not harmful.

These specific proportions are of great importance in producing compounds which will withstand load at high speeds while maintaining low friction and consequently low heat evolution. Under these conditions the bearing materials will be maintained in good condition without scratching or scoring. For example, if the sulfur is in a non-corrosive form or if the amount of corrosive sulfur is substantially below that specified above, the compound will not stand the high bearing pressures. If there be .20 to 1.5 of corrosive sulfur present but insufficient lead, sometimes the load may be carried but there is extreme friction, the temperature rises excessively and the bearing members are found to be discolored, scratched and even deeply scored. In some cases under these conditions the load may not be carried due to the high friction but in any case there is considerable damage done to the bearing members. If the lead-sulfur ratio is properly provided and the lead-sulfur compounds are in sufficient proportion, the load is easily carried with relatively low friction and the heat development is only moderate. The bearing members are found to be in an excellent polished condition, free from scratching and scoring.

In making up the present compounds any source of material containing corrosive sulfur may, of course, be used; for example, heavy petroleum residues, particularly of the type obtained from West Texas and other known crudes. These compounds, however, contain not only corrosive but also ineffective or non-corrosive sulfur and it is therefore necessary to carefully determine the amount of corrosive sulfur in order to blend the sulfur bearing compound in proper proportion. This may be done by first determining the total sulfur and any standard method, for example, by the Bomb method, described in the report of the Committee D-2 of the American Society of Testing Materials, 1928, page 174, and then repeating the determination on a sample which has been deprived of its corrosive sulfur by reaction with finely divided metals such as copper, iron or mercury. The corrosive sulfur may be removed by digesting the compound with finely divided copper in the form of turnings, borings or powder, for a period of twelve hours or so on a steam bath. If desired the temperature may be increased and the time will be proportionately diminished. The sulfur, as will be understood, combines with the metal powder and the second determination of total sulfur by a

standard method now reports only the non-corrosive sulfur, that is to say, the amount which is not capable of reacting with the copper. The difference between the two determinations gives the amount of corrosive sulfur and in making up the blends they should be based only on this proportion.

Other materials may be used as the source of corrosive sulfur, for example, elemental sulfur itself or synthetic organic polysulphides, preferably the pentasulphide or higher polysulphides, or sulfurized oils of unknown constitution which may be made by cooking mineral, animal, vegetable or marine oils with elemental sulfur, or they may be made by treatment of these or similar materials with known sulfurizing agents. Lard oil, pine oils and fish oils produce excellent sulfur-bearing compounds by the above methods but as indicated above, a substantial proportion of the sulfur is almost always in a non-corrosive form and it is again requisite to determine accurately the amount of corrosive sulfur and to use this as a basis for the subsequent blending.

Concentrations of E. P. material	Percent sulfur		Ratio corrosive sulfur to lead	Almen test				
	Total	Corrosive		Weights carried	Final friction	Sudden frictional increase	Pin condition	Final oil temperature
								° C.
0.0% lead oleate, 10% sul. lard oil	1.85	0.356		15	52	7	Poor (scratched)	95
5.0% lead oleate, 10.0% sul. lard oil	1.85	0.356	1:4	15	58	13	Fair (scratched)	85
10.0% lead oleate, 10.0% sul. lard oil	1.85	0.356	1:8	15	48	15	Good (faintly scratched)	70
20.0% lead oleate, 10.0% sul. lard oil	1.85	0.356	1:16	15	27		Excellent (polished)	62
0.0% lead naphthenate, 5.0% thiopinol	1.3	0.5		15	60	5	Poor (scratched)	96
5.0% lead naphthenate, 5.0% thiopinol	1.3	0.5	1:3	15	43	7	do	90
10.0% lead naphthenate, 5.0% thiopinol	1.3	0.5	1:6	15	40	15	Very good	65
10.0% lead naphthenate, 10.0% thiopinol	2.6	1.0	1:3	15	60	7	Poor (scratched)	88
0.0% lead oleate, 0.4% free sulfur	0.6	0.4		15	65	5	Poor (gouged)	90
5.0% lead oleate, 0.4% free sulfur	0.6	0.4	1:3.5	15	60	7	Fair (scratched)	85
10.0% lead oleate, 0.4% free sulfur	0.6	0.4	1:8	15	28		Excellent (polished)	60

The lead compound may be added in any suitably soluble form, for example, as an oleate, naphthenate or sulfonate or as a mixture of any of these substances or as double salts of two of such acids. Acids derived by the oxidation of paraffin or other hydrocarbon waxes may also be used, and as indicated above the sulfur and lead should be in proportions of approximately 1 to 6 or 7 by weight in order to have the substance in stoichiometrical ratio to form lead sulfide, but an excess of lead may be present.

The following tests are given to indicate the nature of the present improved compounds and their improved operation. The tests are made on the Almen testing machine which has been described and illustrated in the National Petroleum News of November 16, 1932. In all tests the same base oil is used in order to make them comparable. The base oil has the following characteristics:

Gravity	19.6
Vis. at 100° F	2371
Vis. at 210° F	94.8
Flash, °F	440
Pour point	10
Per cent total sulfur	.29
Per cent corrosive sulfur	None

In each of the series tests below a specific sulfur containing material is used and data are presented to indicate both the total and the corrosive sulfur content. The amount of lead in its soluble form is also indicated, together with the ratio of lead to corrosive sulfur. The load carried in the test is indicated by the number of weights in accordance with the Almen method referred to above. It is ordinarily observed that the friction starts out at a low figure, increasing as the number of weights is increased. In the case of the preferred compounds the frictional value increases on a smooth curve reaching a maximum as the (last) fifteenth weight is added. The effectiveness of the lubricant, in cases where all 15 weights are carried, is indicated by the value of the final friction. In some instances where an improper ratio of lead to sulfur is used, it will be observed that the friction does not increase smoothly but increases suddenly as the load is increased by the addition of a weight. In the tables the time of the sudden increasing load is indicated by noting the number of the weight which caused the sudden increase in friction. It will be appreciated, as indicated above, that a smooth curve is desirable without any sudden increase of this type especially before the last weight is added. The temperature of the oil under test is likewise indicated and the condition of the pin is also described at the end of the tests.

Ingredients of various quality may be used in the manufacture of these products and as might be expected the properties of the final compound will differ somewhat depending on the grade or class of the different ingredients and the care of manufacture, but where a proper regulation of the relative amounts of lead and sulfur are made in accordance with the present invention, it will be found that a marked improvement in the compound in respect to load-carrying and frictional characteristics, is obtained.

It will be understood that the invention is not to be limited to any theory of the effect of either the sulfur or the lead. It is true that the most effective quantity of these ingredients is the ratio to form lead sulphide but lead sulphide itself is of little or no value. If it is formed during the use of the oil, it is quite different from the addition of preformed sulphide and by the statement that such ingredients are in ratio to form lead sulphide is intended to merely cover the ratio in which the ingredients are used and not to infer a reaction of this or of any other type.

The invention is not to be limited only to the following claims in which it is desired to claim all novelty inherent in the invention.

I claim:

1. An improved lubricant of the extreme pressure type, comprising a heavy hydrocarbon base oil containing about 0.20 to 1.5% of corrosive sulfur and a soluble lead compound in proportion such as to combine to form lead sulfide with substantially no excess of either constituent, the corrosive sulfur being uncombined with lead.

2. An improved lubricant of the extreme pres-

sure type, comprising a heavy hydrocarbon base oil containing about 0.3 to 1.5% of corrosive sulfur and a soluble lead compound in proportion such as to form lead sulfide with substantially no excess of either constituent, the corrosive sulfur being uncombined with lead.

3. An improved lubricating oil of the extreme pressure type, comprising a petroleum oil base together with corrosive sulfur in excess of 0.2% and in the form of one of the following class, free sulfur, sulfurized mineral, animal, vegetable and marine oils, and a soluble lead compound selected from the class of oleates, naphthenates, sulfonates and soaps of acid produced by the oxidation of paraffin wax and present in proportion such as to combine with the corrosive sulfur to form lead sulfide with substantially no excess of either constituent, the corrosive sulfur being uncombined with lead.

4. An improved lubricating composition of the extreme pressure type, comprising a petroleum oil having a viscosity in excess of 100 seconds Saybolt at 210° F. and corrosive sulfur in excess of 0.30% together with lead oleate in proportion such as to combine with the corrosive sulfur to form lead sulfide with substantially no excess of either constituent, the corrosive sulfur being uncombined with lead.

5. An improved lubricating composition of the extreme pressure type, comprising a petroleum oil having a viscosity in excess of 100 seconds Saybolt at 210° F. and corrosive sulfur in excess of 0.30% together with lead naphthenate in proportion such as to combine with the corrosive sulfur to form lead sulfide with substantially no excess of either constituent, the corrosive sulfur being uncombined with lead.

6. An improved lubricating composition of the extreme pressure type, comprising a petroleum oil having a viscosity in excess of 100 seconds Saybolt at 210° F. and corrosive sulfur in excess of 0.30% together with lead sulfonate in proportion such as to combine with the corrosive sulfur to form lead sulfide with substantially no excess of either constituent, the corrosive sulfur being uncombined with lead.

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