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SULPHURIZED OIL

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Our invention relates to sulphurized oils and new compositions of matter used in the preparation thereof.

It has long been known that sulphur compounds when added to lubricating oils impart certain properties to the mixtures which are of great value when these mixtures are used as lubricants for very heavy duty such as is encountered in the lubrication of automotive gears of the hypoid and spiral bevel types and other power transmission gears and for the lubrication of cutting tools such as are used in cutting and threading steel pipe. The exact manner in which the sulphur compounds act to produce these results is not known with any degree of certainty. However, it is not merely a matter of the increased film strength which sulphur compounds impart to lubricating oils since for each sulphur compound that may be added to a lubricating oil to increase its film strength, there is an optimum percentage above which there is no tendency to obtain further increase with greater percentages of the sulphur compound. On the other hand there seems to be no limit to the improvement of a cutting oil that can be obtained by increasing its sulphur content, at least as far as the smoothness of the metal cut obtained with it is concerned.

All sulphur compounds do not have this beneficial effect on lubricants to the same degree as will be brought out in the examples given and to most of those now in use there are certain definite objections. The most common sulphur compounds used for blending with lubricating oils are the sulphuretted glycerides of the unsaturated fatty acids. These will usually contain about twelve percent sulphur. Sulphuretted lard oil is a typical example. These compounds are not entirely satisfactory for blending purposes for several reasons. They are very viscous and hard to handle, raise the pour point of the oil with which they are blended, have a very strong odor of hydrogen sulphide, are irritating to the skin of the operators working with them, are not very stable when in use and do not give a good metal cut when used in a cutting lubricant or a very high film strength when used in an extreme pressure lubricant.

Even with using a large percentage of these sulphur base oils, cutting lubricants are obtained which are rather inefficient as far as cutting qualities are concerned, objectionable on account of odor, irritating to the skin particularly on the knees and elbows of the operator and in case of slight cuts on the hand very liable to cause sores which are slow to heal, are very viscous when cold, are not stable to heat while in use and, as a result break down and thin out. It is mainly due to this fact that the sulphuretted glycerides are inefficient sulphur bases for the preparation of cutting oils. This breaking down results from the excessively high temperature developed in the restricted areas surrounding the cutting tools. This high temperature is the cause of the decomposition of some of the glyceride, which liberates products which have a very irritating effect on the skin. Most of these irritating products come from the decomposition of the glycerine in the sulphur base. It is therefore desirable that a sulphur base should be used which does not contain any glyceride or glycerine. Furthermore some cracking of the petroleum base also takes place in this high temperature zone, giving products which dilute the oil and lessen its efficiency.

An extreme pressure lubricant for gears which is made from the conventional sulphuretted glycerides, such as for example lard oil, has many defects. The film strength is not very high, the pour point of the lubricant is raised 5 degrees to 25 degrees F., depending upon the type of petroleum base oil used, and the oiliness characteristics are not as satisfactory as desired. The glyceride breaks down releasing glycerine which tends to undergo changes resulting in a gum-like deposit which is objectionable in a high quality cutting oil or extreme pressure lubricant.

One object of our invention is to prepare sulphurized oil providing a cutting oil or a lubricant having a high film strength.

Another object of our invention is to provide a sulphurized oil which is stable and devoid of obnoxious odor.

Other and further objects of our invention will appear from the following description.

We have discovered that the sulphuretted organic acids make an excellent sulphur base for blending with lubricants for preparing superior cutting oils and gear lubricants. They are superior to the conventional sulphuretted glycerides of unsaturated fatty acids in a number of ways. To begin with they are in general much less viscous even when containing a much larger percentage of sulphur and are therefore easier to handle. They may be easily and permanently freed from the odor of hydrogen sulphide by blowing for a few minutes with sulphur dioxide after sulphuretting. They are as a group much more stable to heat when used in cutting oils than the sulphuretted glycerides and conse-

quently do not break down and thin out in service as readily. They do not irritate the skin of the operators as do the sulphuretted glyceride blends. Another important advantage of these sulphuretted organic acids is that they are more soluble in petroleum lubricants than the sulphuretted glycerides. The latter have a marked tendency on standing to show sludge-like deposits on the bottom of the containers in which blends of this base and petroleum lubricants have been stored. Lastly, the pour point of blends made with a petroleum lubricant is higher by 10 degrees to 42 degrees F. (depending on the type of lubricant) when a sulphuretted glyceride is used than when a sulphuretted organic acid is used.

The viscosity of the sulphuretted glyceride blends is very much higher at temperatures from 0 degrees to 50 degrees F. than the same blends where the sulphuretted acids of the same glycerides are used. This is a very important consideration for either a cutting oil or a power transmission gear lubricant. In the case of the former it is frequently difficult to obtain a good flow of the cutting oil from the sump of the machines on cold mornings in a shop that is not too-well heated. Under these conditions the machines do poor work and the cutting tools are dulled.

The disadvantages of a relatively high pour test and high viscosity at cold weather temperatures in the case of gear lubricants causes excess loss of power in overcoming the internal friction of the lubricant and difficulty in shifting of gears in the case of automobile transmission gears.

A number of examples of the sulphuretted organic acid type of blends of lubricants used for cutting oils and gear lubricants will be described. Similar blends containing the same amount of added sulphur but made with a sulphuretted glyceride of an unsaturated fatty acid will also be described. The superior results of the tests on the former blends will demonstrate the improvement obtained by the use of these sulphur bases over the well-known sulphuretted glycerides.

The method of testing and comparing the efficiency of the cutting oils in question consisted in the use of a 2'' Toledo thread cutting machine under a set of standard commercial operating conditions with the different oils and comparing the threads obtained with each. The smoothness of the ridges and the tearing or lack of tearing in the troughs was noted and the cutting oil graded accordingly. Note was also made of the odor of the cutting oils, since a cutting oil might be quite efficient as a lubricant but have such an obnoxious odor that it could not be used. The comparative cooling properties of the different oils was also noted by observing the tendency of the oil to smoke while in use and also by the temperature of the nipple that had been threaded. This heating and smoking tendency of the oil is directly related to the efficiency of the lubricant as it has been noticed that the more heating and smoking that accompanies the cutting, the poorer will be the finished thread.

The method of testing the new sulphur bases to determine the relative value they possessed as extreme pressure compounds compared to the sulphuretted glycerides, consisted in making blends with a heavy petroleum lubricating oil in which the same quantity of added sulphur was used in each and determining the film strengths of these blends on the Timken machine. This is a device which was developed by the Timken Roller Bearing Co. for comparing film strengths of extreme pressure lubricants and is fully described in the literature of the art.

Example #1.—Oleic acid is heated to 340 degrees F. and 12% sulphur by weight is added with stirring until the reaction ceases. A blend of this sulphur base with a low viscosity lubricating oil in the proportion of seven parts by volume of 100 S. S. U. viscosity at 100 degrees F. black oil to three parts by volume of the sulphur base which is equivalent to adding 3.6% sulphur, gives an excellent cutting oil which is far superior with respect to smoothness of thread obtained, to a similar blend in which sulphuretted lard oil is used in the same proportion and has the further advantage of being practically odorless whereas the sulphuretted lard oil blend has a very obnoxious odor. The thread obtained with the former blend is very smooth and shows no tearing while the thread obtained with the latter blend is decidedly rough.

Example #2.—A mixture of organic acids obtained as a by-product from pine wood and which consists of roughly 30% rosin acids, 50% of unsaturated fatty acids, and 20% sterols is heated to 375 degrees F. and sufficient sulphur is slowly added with stirring so that the resulting compound contains at least 25% sulphur. A blend of 8% of this sulphur base, which is equivalent to 2% of sulphur, with a low viscosity petroleum lubricating oil such as 100 S. S. U. at 100 degrees F. black oil gives an excellent cutting oil while a blend containing 16% of this sulphur base, which is equivalent to 4% sulphur, gives a very superior cutting oil. If a blend containing 20% to 25% of this sulphur base, which is equivalent to 5% to 6¼% sulphur, is made with a lubricating oil, a cutting oil is obtained that gives a far smoother thread when used on a thread cutting machine than the most expensive and best commercial cutting oils now available.

A blend prepared by mixing 13 parts of this sulphur base and 87 parts of the above mentioned black oil was used in a 2'' Toledo thread cutting machine for three months. This is a thread cutting machine in which about 3 gallons of the cutting lubricant is poured into a sump from where it is pumped over the cutting tools and then is allowed to run back into the sump and is thus used indefinitely. After three months use during which time over 1,000 threads were cut and only enough fresh oil was added to make up for what was lost by mechanical causes, a sample of the cutting oil was removed from the machine and tested. The sulphur content of the original was 3.7% and of the used oil, 3.3%. The viscosity of the original was 184 S. S. U. at 100 degrees F. The viscosity of the used oil was 186 S. S. U. at 100 degrees F. A thread cut with the used oil was smoother than a thread cut with a fresh sample of the best commercial cutting oil available to the market. This shows the remarkable stability of this new oil. The life of the cutting tools was four times as great as it was with the sulphuretted lard oil cutting oils which had been previously in use in the same machine. The operators at no time experienced skin trouble when using this new cutting oil in contrast to the irritation caused by the old type lubricant. The pour point of this new oil is below —15 degrees F., while the pour point on a similar blend where sulphuretted lard oil is used in the same proportion is +10 degrees F. The odor of the new cutting oil was much less objectionable than the odor of the sulphuretted lard oil cutting lubricant.

Example #3.—Rosin oil, which consists chiefly of abietic and homologous acids, was sulphuretted at 380 degrees F. until a compound containing 26% sulphur was contained. A blend of this sulphur base and 100 S. S. U. at 100 degrees F. black oil in which sufficient of the sulphur base is used to give 1% up to 6% of added sulphur in the finished blend has the properties of an excellent cutting oil. Rosin, itself, which is mainly abietic acid, may be sulphuretted and used as a sulphur base for preparing cutting oils; however, it is not so desirable because a portion of the sulphuretted rosin is not very soluble in petroleum oil.

A very excellent extreme pressure lubricant may be prepared from any of the above mentioned sulphur bases which in comparison with other sulphur bases are much superior in regard to film strength.

Example #4.—A blend consisting of 7% of sulphuretted pine wood acids of Example #2, which is equivalent to 1.6% of added sulphur, with 83% of steam refined cylinder stock and 10% of a 200 S. S. U. viscosity at 100 degrees F. neutral oil yields a mixture of 140 S. S. U. viscosity at 210 degrees F. which is a very superior transmission and differential gear lubricant. Its film strength as determined on the Timken machine is 66.8 lbs. or about 46,760 lbs. per square inch rubbing surface. The same viscosity blend when made with a sulphuretted glyceride type of sulphur base such as is prepared from lard oil in which 13% of this base is used to obtain the same amount of added sulphur (1.6%) has a film strength by the Timken machine test method of 30 lbs. or 21,000 lbs. per square inch.

The saturated organic acids which can be heated to 400 degrees F. without decomposition may be sulphuretted and used in this invention but are generally not as satisfactory as the unsaturated organic acids. Some stearic acid was made to take up 12% sulphur by sulphuretting at 400 degrees to 425 degrees F. and a cutting oil prepared as in Examples 1 to 3 which on testing gave a fair thread, but this particular sulphur base raised the pour test, making the blend less satisfactory for use in a cutting oil than the blends of sulphuretted, unsaturated fatty acids.

We feel reasonably sure that the extraordinarily fine results, obtained with the sulphuretted pine wood acid blends of cuttings oils, are largely due to the fact that it is possible to incorporate a relatively large quantity of sulphur in these types of organic acids. We believe that it is the last 25% of the sulphur added to these acids which, combined with the oiliness feature imparted by the carboxyl group of the acids, contributes mainly to the effectiveness of this sulphur base for the preparation of cutting oils. This is because the sulphur that is added to a compound near its saturation point is less firmly held than that which is first taken up. The sulphur that is loosely held appears to be the effective part of a cutting lubricant.

In sulphuretting, we find that it is best to employ a temperature between 340° F. and 400° F. Between this temperature range, we are enabled to obtain the maximum percentage of sulphur. It is to be remembered, of course, that the sulphuretting action may take place at other temperatures but the best results are obtained between the temperature range above specified.

In preparing a sulphur base for a gear lubricant from this type of organic base, a more satisfactory product is obtained if somewhat less than the amount of sulphur required to saturate the organic base is used as this will reduce its corrosiveness.

Some highly unsaturated fatty acids such as for instance those which are obtained from fish oils cannot be readily sulphuretted so that an oil soluble derivative is obtained, but if these fatty acids are first partially hydrogenated, a very satisfactory sulphur base for cutting oils may be made from them.

Any means of removing hydrogen sulphide from the sulphur bases after sulphuretting may be employed. This may require the use of a weak oxidizing or reducing agent or treatment with gaseous sulphur dioxide or any other means that gives satisfactory results. The means for the removal of hydrogen sulphide from the sulphur bases, however, are not a part of this invention.

While no specific limit to the percentage of the sulphur base to be used in preparing the different lubricants referred to in the examples has been drawn, it may be stated that in preparing a cutting oil to be used without first diluting, not less than 1% or more than 4% of added sulphur, in the form of the sulphur base in question, is required. If a cutting oil concentrate is prepared that is to be diluted before use, a much higher percentage of sulphur may be used in the blend. The straight sulphuretted organic acid may be used also for this purpose.

In the case of preparing a lubricant for heavy duty gears as little as .5% of added sulphur may be used for the mild extreme pressure lubricant up to 2.5% of added sulphur for the more rugged extreme pressure lubricant. More is seldom necessary.

A small quantity such as .1% to .2% of sulphur in the form of one of these sulphur bases may be added to a crank case lubricant to improve the film strength and oiliness of these lubricants.

The above ratios of sulphur base to petroleum oil for its different uses are not intended to limit the scope of this invention since smaller or larger quantities may be used in any case with results which are partially satisfactory. They are given because generally speaking the optimum results can be obtained by the use of ratios within the limits that are suggested.

The hydrocarbon oils which are used in blending with the sulphuretted organic acid bases for the preparation of the various sulphuretted lubricants are not to be limited to the hydrocarbon oils cited in the examples but are to include any hydrocarbon oil of any type or viscosity such as may be required by the lubricant in question.

Having thus described our invention, what we claim is:

1. A lubricant which is corrosive to the copper strip test comprising in combination a hydrocarbon oil and a base prepared by sulphurizing unsaturated fatty acid obtained from wood oil.

2. A lubricant including in combination a hydrocarbon oil and from 1 to 4 per cent of a sulphurized organic acid obtained as a by-product from wood, said sulphurized organic acid containing at least 25 per cent of sulphur in chemical combination.

3. A lubricant including in combination a hydrocarbon oil and from 1 to 4 per cent of a sulphurized organic acid obtained as a by-product from pine wood, said sulphurized organic acid containing at least 25 per cent of sulphur in chemical combination.

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