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SULPHURIZED OIL

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1 Claim. (Cl. 87-9)

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, with respect to the cutting lubricants, act to produce these results is not known with any degree of certainty. It is more than 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 herebelow 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 usually contain about 12% sulphur. Sulphuretted lard oil is a typical example. These compounds are not entirely satisfactory for blending purposes for several reasons. The sulphuretted glycerides are very viscous and hard to handle, and 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 as stable as desired when in use and do not give a good cut when used in a cutting lubricant and do not give 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 of the operator and in case of slight cuts on the hand,

cause sores difficult to heal, are very viscous when cold, and are not stable to heat while in use, as they break down and thin out.

An extreme pressure lubricant for gears which is made from the conventional sulphuretted glycerides, such as for example lard oil, has many defects. In the first place, this type of sulphur base blend is not as stable as is desired to the copper strip corrosion test, which some automobile manufacturers now require for sulphur base lubricants. Secondly, the film strength is not very high, and last, the pour point of the lubricant is raised 5 degrees to 25 degrees F., depending upon the type of petroleum base oil used.

We have discovered that the sulphuretted monohydric and dihydric alcohol esters of organic acids make excellent sulphur bases 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 than the sulphuretted glycerides and consequently, do not break down and thin out in service as readily. When the glyceride breaks down glycerine is released which forms gum and is generally objectionable. They do not irritate the skin of the operators. They are cheaper because about twice as much sulphur may be added to this type of compound as can be added to the glycerides and thus give a more concentrated base oil. Another important advantage of these sulphuretted monohydric and dihydric alcohol esters is that they are more soluble in petroleum lubricants than the sulphuretted glycerides. The latter have a marked tendency to show a sludge-like deposit on the bottom of the container in which a blend of this base and a petroleum lubricant has stood for some time. Lastly, the pour point of blends made with a petroleum lubricant are higher by 10 degrees to 25 degrees F. (depending on the type of lubricant) when a sulphuretted glyceride is used than when a sulphuretted monohydric alcohol ester 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 monohydric alcohol

esters of the same acids are used. This is a very important factor when considering 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 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 ester type of blends for heavy duty lubricants is listed below for the purpose of illustrating this invention.

Example No. 1.—Commercially pure methyl oleate was heated to 380 degrees F. and sulphur was slowly added with stirring. After sufficient sulphur had been added to give a compound containing 20% of sulphur, the temperature was raised to 420 degrees F. and about 6% more of sulphur was taken up by the ester. The product was blown with sulphur dioxide at 380 degrees F. for two minutes to remove hydrogen sulphide. On cooling, the ester was found to be much less viscous than the glyceride after sulphuretting. The glyceride cannot be made to take up more than 12% or 13% of sulphur and cannot be heated to so high a temperature without breaking down. The sulphuretted ester, on blending with a 100 S. S. U. viscosity black oil to the extent so that 2% of sulphur (equal to 8% of the sulphur base) is added to the petroleum base, gives a superior cutting lubricant which is very stable to heat, flows readily at -14 degrees F., does not thin out with use, has practically no odor, does not irritate the skin of the operator, and when used with a cutting machine gives a very smooth cut. The same type of cutting oil made with the sulphuretted glyceride in which enough of the sulphuretted glyceride (16% sulphuretted lard oil and 84% of the same black oil) is used to give the same amount of added sulphur has a very obnoxious odor due to hydrogen sulphide that is released, has a tendency to thin out more readily in use, probably because it is less stable to heat, is thicker when cold having a pour point of 15 degrees F., and gives a rougher machined surface when used with a cutting machine which in turn means a quicker dulling of the cutting tool, and is extremely irritating to the skin. A cutting oil made with the same viscosity black oil and sufficient sulphuretted methyl oleate to impart 4% or 5% of added sulphur (equal to 16% or 20% of the sulphur base) gave a most extraordinarily efficient cutting lubricant. When such a blend is used with a thread cutting machine a thread of almost velvety smoothness is obtained.

Example No. 2.—Commercially pure ethyl abietate was heated to 370 degrees F. and sulphur was slowly added with stirring and raising of the temperature to 400 degrees F. until a product was obtained containing 27% sulphur. This sulphur base, blended with a 100 S. S. U. viscosity black oil to the extent that 5% of sulphur (equal to about 20% of sulphur base) is added to the blend, gave an excellent cutting oil which was practically odorless and which had a very low cold test and flowed readily at 0 degrees F. It was stable to heat and did not thin out in use, and did not irritate the hands of the operator.

Example No. 3.—Rosin oil which is a mixture of aromatic acids similar to abietic acid was esterified with methyl alcohol and the methyl esters sulphuretted by heating to 380 degrees F. and slowly stirring in sulphur until a compound containing 25% of sulphur was obtained. This sulphur base when blended with a 100 S. S. U. viscosity black oil to the extent that about 4% of sulphur (equal to 16% of sulphur base) was added to the blend, made an economical and very efficient cutting oil.

Example No. 4.—A mixture of organic acids obtained as a by-product from pine wood processing and which consists of about 30% of "rosin acids," 50% unsaturated fatty acids, and 20% of higher alcohols of the sterol type was esterified in the usual manner by refluxing with an excess of methyl alcohol using hydrochloric acid as a catalyst and the methyl esters and higher molecular weight esters thus resulting were then sulphuretted by heating to 380 to 400 degrees F. and by slowly adding sulphur with stirring. When the product contained 25% sulphur the temperature was dropped to 375 degrees F. and sulphur dioxide was blown into the compound for two minutes to remove excess hydrogen sulphide and to stabilize it. Air blowing for one minute then removed the excess of sulphur dioxide. Blends were made with 100 S. S. U. viscosity black oil containing 2%, 4%, and 6% of added sulphur. This required 8%, 16% and 24% respectively of sulphur base. These blends were tested for their efficiency as cutting oils by cutting threads under a standard set of operating conditions on a Toledo 2" thread cutting machine and comparing the threads thus obtained with threads cut with an expensive competitive cutting oil. The blend containing 2% of sulphur gave a thread slightly inferior to the competitive cutting oil but the 4% blend gave a thread which was its equal and the 6% blend gave a much superior thread.

These blends all gave threads that were far superior in evenness and smoothness to the threads obtained when sulphuretted lard oil was used in the lubricant even though as much as 30% of the sulphuretted lard oil was contained in the lubricant. In addition, they were quite free of all odor and during a period of several weeks use did not in any way prove irritating to the skin of the operators. On cold mornings there was no difficulty encountered in obtaining a good flow of lubricant in contrast to the viscosity of the sulphuretted lard oil blends under the same conditions. There also appeared to be no tendency towards breaking down and thinning out of the lubricant after a long period of use as was the case with the sulphuretted lard oil blends. The quality of the threads obtained after a long period of use for the oil was as high as when the oil was fresh.

The quality of thread is judged by the smoothness of the ridges and the lack of any pulling of the metal in the troughs.

Example No. 5.—A transmission gear lubricant prepared by blending 8% of the sulphuretted methyl oleate (equal to 1.6% of added sulphur) of Example No. 1 with 13% of 220 pale oil and 77% of steam refined stock gave an excellent extreme pressure lubricant. This lubricant had a film strength of 33 lbs. on the Timken machine which is a standard testing machine for measuring film strength. This is equal to approximately 23,000 lbs. per square inch of rubbing surface. A transmission gear lubricant prepared by blending 13% of sulphuretted lard oil (equal to 1.6%

added sulphur) with 12% of 220 pale oil and 75% of steam refined stock gave a film strength of 27 lbs. on the Timken machine. This is equal to about 19,100 lbs. per square inch. The odor of the former blend was pleasing while the latter smelled of hydrogen sulphide. A copper strip corrosion test at 210 degrees F. for one hour gave much less discoloration with the former lubricant than with the latter.

Monohydric esters of the highly unsaturated fatty acids such as are found in fish oils cannot be readily sulphuretted so that an oil soluble derivative is obtained, but if the fish oil or esters therefrom are first partially hydrogenated, a very satisfactory sulphur base for cutting oils can be made from them.

While examples of esters of methyl and ethyl and the high molecular weight alcohols in the pine wood acids of Example No. 4 only are cited, it is to be remembered that other monohydric alcohols such as propyl, butyl, and higher alcohols can also be used for preparing the esters which are to be sulphuretted. Furthermore, the esters of dihydric alcohols such as glycol mono or di-oleate might also be used with satisfactory results. Naturally occurring mono and dihydric esters may be employed in this invention.

The esters of the saturated fatty acids may also be sulphuretted and used in this invention. It is necessary to use somewhat higher temperatures (400 degrees to 425 degrees F.) to sulphuret this type of ester since most of the sulphur reacting with the saturated ester must do so by replacing hydrogen. The sulphuretted esters of the saturated fatty acids are not so satisfactory as the sulphuretted esters of the unsaturated fatty acids for two reasons. They will not take up nearly as much sulphur (usually only about 10%) and have a relatively high pour point.

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 as described in Example No. 4 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 limits to the percentage of the sulphur 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 ester 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 using the ratios within the limits that are suggested.

The hydrocarbon oils which are used in blending with the sulphuretted ester 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:

A lubricating oil comprising in combination a major proportion of a hydrocarbon oil and a minor proportion of the sulphurized esters obtained by esterifying with a monohydric or dihydric alcohol the fatty acids obtained from processing pine wood, and then sulphurizing these esters.

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