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SULPHURIZED LUBRICANT

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6 Claims. (Cl. 252—46)

This invention relates to lubricants, including both oils and greases, which contain sulphur to impart extreme pressure characteristics such as improved film strength, load-carrying capacity and wear resistance. The object of the invention primarily is to provide a product and a method of procedure which will avoid difficulties heretofore experienced such as the separation of the sulphur after sulphurization or the formation of insoluble or otherwise objectionable sludges, or the development of substantial corrosiveness and the like when in use or when subjected to somewhat elevated temperatures.

It is also an object of this invention to overcome serious operating difficulties which have been heretofore encountered in attempting to sulphurize mineral oils directly.

Briefly stated, the invention resides in the employment of small proportions of rosin or rosin oil or other rosin fractions or rosin acids or "pine" acids, in sulphurized mineral lubricating oils and in connection with processes for producing such oils. All of these rosin materials or pine acids contain large proportions of abietic acids.

By employing rosin or rosin materials containing these rosin acids, the acceptability of the lubricating oil for sulphur, that is the capacity of the oil to receive and retain sulphur, is improved, so that the optimum sulphur content for these oils may be increased and whereby the optimum operating ranges for the sulphurizing step may be increased with respect to both time and temperature of treatment.

In producing lubricants of this character, the mineral oil itself ordinarily has a sulphur acceptability characteristic for about 2% to 3% of sulphur based on the oil. Where rosin or rosin oil or the like is added to the oil in small quantities, for example 1% to 2%, the acceptability of the oil itself for sulphur is increased by about 1% or sometimes 2% of additional sulphur. At the same time the rosin material added will accept about 40% of sulphur based upon the content of rosin material. By the expression "acceptability for sulphur" is meant the capacity to receive sulphur in solution or in chemical combination according as the actual fact may be, without substantially increasing the sludging tendencies of the sulphurized oil over the sludging tendencies of the original mineral lubricating oil employed. Observing these principles, the sulphur content for a finished lubricating oil will normally be in the range of about 1% to 6% or 7% of the composition, and the rosin content will normally be in the range of about 0.5% to 6% or 7%. It will be appreciated that a sulphur content of about 2% to 5%, where about 3% or more sulphur is present, is accounted for by the solvent power of the oil itself for sulphur, including the increased acceptability of the oil for sulphur where rosin materials are present.

Therefore, invention resides in these proportions. Also lubricating concentrates, which might possibly be used as lubricants in certain connections, may be made containing increased quantities of both rosin material and sulphur, which concentrates may be subsequently diluted with oil to produce the desired finished product. These concentrates will extend up from the limits of 6% or 7% for each of the sulphur and rosin materials in a finished lubricant to as much as 20% sulphur with 45% rosin and only 35% mineral oil in the concentrate. As the sulphur content is increased, it is necessary to increase the content of rosin material correspondingly in order to avoid excessive sludging of the product, that is sludging appreciably greater than the sludging property of the unmodified lubricating oil itself.

Therefore, the invention resides further in lubricants comprising mineral lubricating oils, from about 0.5% to about 45% of rosin materials and from about 1% or 2% to about 20% of sulphur in solution in the lubricant. The invention further resides in such lubricants wherein the rosin content is increased as the sulphur content is increased to insure against substantial sludging tendencies. Thus, the invention resides also in lubricants comprising primarily mineral oil with about 10% or 12% sulphur and about 20% rosin material up to about 20% sulphur with 45% rosin materials. The invention also resides in methods of preparing such lubricants wherein the materials are heated at elevated temperatures in the order of 250° F. to 400° F. to obtain the desired solution or chemical combination of the sulphur. The invention resides further in so treating the materials by combining the rosin material with lubricating oil and then introducing the sulphur, the batch being heated for an extended time to accomplish the proper incorporation of the sulphur.

In operating according to the present invention, the rosin or abietic acid material in required amount (for example 1%) is added to mineral lubricating oil, and preferably to this mixture there is added the required amount of sulphur (for example 3%) for the sulphurized lubricant sought to be produced. Any type of mineral

lubricating oil may be employed, the only difference being that different mineral lubricating oils possess slightly different degrees of acceptability for sulphur. The rosin material may be any commercial material containing abietic acid such as rosin, "kidney" rosin oil, commercial abietic acids, "pine acids" and the like. These materials are then heated together in a suitable kettle, preferably a pressure kettle, whereby superatmospheric pressures may be obtained if desired, any suitable heating means being employed such as fire or steam coils. The contents of the kettle are raised to temperatures which may vary somewhat in accordance with the particular materials being employed. Temperatures between about 250° F. and 400° F. are employed. The temperature is maintained within that range, for example around 300° F. or about 290° F. to 310° F., with agitation for a sufficient length of time to effect the degree of sulphurization which can be accomplished with the sulphur which has been added. By operating with these materials, the length of time for treatment may be increased beyond times heretofore ordinarily used for sulphurization and, by reason of the presence of the rosin material, the extent of sulphurization is increased without producing products having excessive sludging tendencies, as above indicated. The time of treatment will vary ordinarily within the range of about three hours to nine hours, e. g. six hours. By heating under these conditions, the sulphur apparently is primarily chemically combined with the rosin oil, and also with the lubricating oil to the extent of the 2% to 5% which the lubricating oil will accept as has been indicated. Secondarily, some of the sulphur apparently is physically combined in the mixture, possibly as by solution in the oil or in the rosin material. This incorporation of the sulphur into the lubricant is generally herein referred to as "solution," which term is intended to include the solution or chemical union or both according to whatever condition exists by reason of the treatment at elevated temperature.

The resultant oils containing the proper proportion of sulphur and rosin materials as indicated are stable from the standpoint of their sulphur content, and in use do not sludge appreciably beyond the normal sludging tendency of the unmodified lubricating oil itself. The relative proportions of sulphur and rosin materials to be employed to obtain these stable non-sludging oils were indicated above, it being necessary, as also indicated above, that the proportions of rosin materials be increased adequately as the sulphur is increased to insure proper union or solution of the sulphur with the mixture of mineral lubricating oil and rosin materials in order to form the stable products having the desired substantially non-sludging tendencies.

In general, when producing a finished lubricating oil, it is preferred to limit the sulphur content, and consequently the rosin content, to relatively low proportions, inasmuch as these ordinarily are adequate to impart the desired extreme pressure characteristics sought in lubricating oils of this type, for example in the preparation of hypoid gear lubricants. This desired limitation of the abietic acid of the rosin materials may be easily accomplished for the reason that the abietic acid molecules ($C_{19}H_{29}COOH$) are capable of accepting one or many sulphur atoms according to the degree of sulphurization required in the final product. Thus, for a finished oil a typical average rosin acid or rosin material content to be employed would be about 1% or within a practical range of probably about 1% to about 2%. In this case, from 1% to 3% or 4% of sulphur for each percent of rosin may be introduced, the mineral oil itself taking up some of the sulphur. Typical examples will contain:

Mineral lubricating oil	About 98.5% to about 93%
Rosin	About 0.5% to about 2%
Sulphur	About 1% to about 5%

Instead of preparing the finished lubricant containing only 1% or 2% rosin and 3% to 5% sulphur, a finished oil may be produced containing more rosin and more sulphur if desired. For example, up to 6% or 7% or possibly a little more of each of the sulphur and rosin material. In many instances, however, it is preferred to manufacture lubricating concentrates containing much smaller proportions of lubricating oil, the additional lubricating oil to be blended into the concentrate at some future time. Thus, a concentrate containing about 40% or possibly a little more of rosin material, about 40% of lubricating oil and about 20% of sulphur may be produced. It is to be recognized that here, after accounting for the sulphur taken up by the lubricating oil itself, the remaining sulphur content ordinarily should not exceed about 40% of the rosin material content. While it is possible at least for some uses, that the sulphur content based on the rosin material may be greater than 40%, nevertheless on the average this sulphur limit should be observed where stable substantially non-sludging products are required. On this basis, a rosin material content of about 20% of the total would support a sulphur content, including that accepted by the oil itself, of about 12%. Of course, these limits are not critical because of the fact that, as above indicated, each abietic acid molecule is capable of accepting not only one but many sulphur molecules. In general, however, the invention lies in the incorporation of sulphur, as above indicated, into rosin and mineral oil mixtures wherein the maximum of rosin material indicated for any given sulphur content is employed so as to insure stable substantially non-sludging products, the percentage content of rosin being in the order of from 0.5% to 40% or possibly 45% with a corresponding sulphur content within the range of about 1% to about 20%, the rosin material content increasing as the sulphur increases, it being recognized that from about 2% to perhaps 5% of sulphur is accepted by the mineral lubricating oil itself.

With respect to rosin materials which may be used according to this invention, kidney rosin oil, which is a rosin distillation product well known in the industry, has been indicated above and is generally preferred, especially for sake of convenience. Nevertheless, I may also use other sources of rosin acids or "pine acids," such as wood rosin, gum rosin, other rosin oils than that mentioned, commercial rosin acids or abietic acids, pimaric acid, pseudo-pimaric acid and the various distillation products of these materials in crude or purified form, and also various modified rosin acids, such as modified rosins or modified abietic acids or derivatives thereof known on the market. Rosin acids or pine acids are generally understood to include primarily abietic acids, and also pimaric acid, pseudo-pimaric acid, sapinic acid and the like and various isomers and

polymers thereof present in the naturally-occurring rosin and its fractions, such as rosin oil.

Lubricating oils which may be employed include any of the well known petroleum lubricating oils, and may also be extended to include kindred products from the distillation of shale, peat or coal. Ordinarily mineral lubricating oils would be employed, such as ordinary types of acid treated western or naphthenic base lubricating oils or Mid-Continent oils. Similarly various Pennsylvania or paraffinic type oils, such as Pennsylvania neutral oils and the like, may be used, or various blends of these oils, such as mixtures of Mid-Continent steam refined oils, Pennsylvania neutral oils and western lubricating oils of the naphthenic type such as above mentioned, these being employed in approximately equal proportions or otherwise as may seem fitting. Also the heavily solvent treated oils of high paraffinic oil content, or other highly refined paraffinic type oils, may be used alone or in admixture with other lubricating oils as above indicated.

In the heat treating operation the temperature on the average will be around 300° F. or from perhaps 290° F. to 310° F. Ordinarily the rosin oil is added to the lubricating oil in the kettle, and if other rosin products, such as rosin itself or commercial abietic acid, are used, the temperature may be raised with agitation until solution of the rosin material is effected. The powdered flowers or sulphur are ordinarily added to the oil and rosin product solution after the latter has reached the operating temperature, for example 300° F. Agitation is maintained for an appropriate period of time, for example six hours, until the sulphur which has been added, for example 2.5%, has combined with the oil. In a particular instance, 965 parts of bright filtered Pennsylvania lubricating oil stock was combined with 10 parts (1%) of the rosin distillation product known as No. 56 kidney rosin oil, and this mixture then heated to 300° F. to 310° F., whereupon 25 parts of flowers of sulphur (2.5%) were added and the heating continued with agitation for six hours. This sulphurized material was cooled and 5% of lead naphthenate was added as a corrosion inhibitor.

While variations in temperature, and in sulphur content, and in the time of treatment are sometimes necessary according to the oils used or the rosin material incorporated or the amount of sulphur employed, these will be readily ascertainable by any skilled lubricant manufacturing operator, especially because of the fact that this procedure involving the employment of rosin oil or other abietic acid or similar rosin acid-containing material, has such a wide range of permissible or optimum heating conditions that no difficulty whatever will be experienced. In other words, regardless of the oil stock, or the amount of sulphur, the temperature limits will usually lie within the range of 250° F. to 400° F. above indicated, and the heating time will nearly always be found to be within 3 to 9 hours or at least within a maximum range of 2 to 16 hours. Completion of the operation is readily determinable by tests outlined below.

For every particular mixture of oil, rosin and sulphur there is an optimum length of time to react at a given temperature in order to get maximum load-carrying capacity and minimum sludging. Too short a time of reacting gives oil which is too corrosive and has a tendency to deposit sulphur. Too long a time leads to increased tendency to sludge and loss in load-carrying capacity. The optimum time is determined by removing samples of an experimental mix and adding corrosion inhibitor, (lead naphthenate) and determining load-carrying capacity and tendency to sludge and corrosiveness to steel. From those results the time required for a given mixture is chosen. The corrosive effect and sludge-forming tendencies of the oil are determined arbitrarily by adding 5% of lead naphthenate to the oil as a corrosion inhibitor, immersing polished steel strips in portions of the oil with and without the addition of 5% of distilled water to the oil, maintaining a temperature of about 180° F. for 16 hours, and then observing the effect of such treatments on the steel strips. An oil to be considered fully acceptable should not deposit any sludge-like material or blacken the steel strips to any noticeable extent, even in the presence of water.

The operations may be modified in certain connections if desired, for example by the use of catalysts such as halogens or the various metallic halides (e. g. 0.1% of preferably alkali halides) to increase the reaction rate, or by the use of closed kettles to eliminate air, as may be convenient to speed up the reactions especially where highly refined oils are employed such as highly solvent treated naphthenic base oils or highly purified paraffinic base oils.

It will be recognized, of course, that where a given percentage of sulphur is indicated as being added to the charge, a small proportion of the sulphur is normally lost as hydrogen sulphide during the operation, and a correspondingly smaller proportion of sulphur actually enters into the composition.

With the addition of a suitable corrosion inhibitor, for example 5% of lead naphthenate as in the example given above, these products have been found non-corrosive to steel under normal operating conditions and to have load-carrying capacity of at least 550 pounds (scale reading) as measured by the S. A. E. extreme pressure lubricants tester at 1000 R. P. M. with a loading rate of 83.5 pounds per second and a rubbing ratio of 14.6 to 1. Such a tester is found described in the S. A. E. Journal for July, 1936, pages 293 to 290 (vol. 39).

Products according to the invention do not offer the objections of precipitating sulphur or sulphur crystals or yielding insoluble sludges upon standing or in operation, and when the corrosion inhibitor agent is introduced, they yield material also non-corrosive to steel in the presence of water. With reference to corrosion inhibitors, the percentage of lead naphthenate employed may be varied from the 5% mentioned within a range between about 4% and 10%. As substitutes for lead naphthenates, other soaps such as zinc naphthenate, magnesium, naphthenate and lead oleate may be used, and other corrosion inhibiting materials such as zinc octyl thiophosphate may sometimes be employed.

It is to be understood that these disclosures are illustrative of the generic invention hereof and are not to be taken as limiting except as required by the prior art.

I claim:

1. A lubricating concentrate comprising in the neighborhood of 45% rosin materials, 20% sulphur and 35% mineral lubricating oil.

2. A lubricant comprising mineral lubricating oil, rosin materials in solution in the oil, the rosin materials containing sulphur approximating 40%

of said rosin materials, and the oil containing additional amounts of sulphur in solution therein in the order of 2% to 5%.

3. A lubricant comprising mineral lubricating oil and from about 0.5% to 45% of rosin materials, and sulphur in solution in the lubricant in the order of 40% based on the rosin content.

4. A lubricant according to claim 10 containing in addition from 2% to 5% of sulphur in solution in the oil calculated on the basis of the oil content of the lubricant.

5. A lubricating composition comprising mineral lubricating oil, about 1% of rosin materials containing abietic acid and about 3% of sulphur in solution in the lubricant.

6. A lubricating oil comprising about 96% mineral lubricating oil, about 1% of rosin material and about 2% to 5% of sulphur incorporated in the lubricant.

RALPH A. POTTER.

CERTIFICATE OF CORRECTION.

Patent No. 2,246,415. June 17, 1941.

RALPH A. POTTER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 40, for "1% to 2%" read --1% or 2%--; page 4, first column, line 8, claim 4, for the claim reference numeral "10" read --3--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of November, A. D. 1941.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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