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LUBRICANT

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1 Claim. (Cl. 252—48)

Our invention relates to sulfur-containing lubricants and more particularly to a lubricant containing a sulfur-bearing addition agent, substantially non-corrosive to the newer types of bearing metals now used in present-day automotive vehicles.

Modern automobile engines are now constructed with bearings containing cadmium and copper-lead mixtures as well as with bearings of high lead content. These new bearings, while possessing certain mechanical advantages over the old tin-babbitt bearings, are more susceptible to corrosion. Oxidation and decomposition products of the lubricant react with these bearings and often cause failure through corrosion.

One object of our invention is to provide a lubricant containing a new type of sulfur compound which will impart increased film strength to the lubricant while being substantially non-corrosive to the new-type bearing metals.

Another object of our invention is to provide a sulfur-containing addition agent which is at once a film-strength improver and a corrosion inhibitor.

Another object of our invention is to provide a lubricant having increased oiliness characteristics and color stability.

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

In general, our invention comprises the use of a sulfurized poly-isobutylene added in small quantities to hydrocarbon oils. As small a quantity as .05 of 1 per cent of our new sulfur compound, added to a lubricant, increases its resistance to oxidation and corrosiveness. As much as 20 per cent of the compound may be added to a lubricant with beneficial results with respect to its film strength and oiliness properties, although it is seldom that more than 2 per cent need be used for a crankcase lubricant. A lubricant containing from 2 to 20 per cent makes an admirable cutting oil or an extreme pressure lubricant.

The material which we sulfurize to obtain the addition agent of our invention is poly-isobutylene, a mixture of di, tri, tetra, and other isobutylenes. This material may be made by the action of sulfuric acid on butylene and/or isobutylene. The material produced in this reaction is a mixture of isomers but it may be substantially pure di or tri or tetra-isobutylene or the mixtures may have an average molecular formula of C_8H_{16} or $C_{12}H_{24}$ or $C_{16}H_{32}$ but never exceeding 32 carbon atoms per molecule. In this invention we refer to these materials as poly-isobutylene and include the isobutylene polymer derivatives up to those with a molecular weight of 500. The higher molecular weight materials upon sulfurization give rubber like compositions which are not contemplated in our invention. The rubber like materials have a tendency to be insoluble in lubricating oil and will gum or coat certain metals found in engines during commercial use. The molecule is unsaturated in that it has a double bond between two carbon atoms. The sulfur combines with the molecule at the double bond. The boiling point of the product of sulfurization of this material is high enough that it will not distill off when used as a lubricant.

In sulfurizing the poly-isobutylene or the substantially pure material, we may use elemental sulfur or various compounds of sulfur, including sulfur monochloride, sulfur dichloride, phosphorus pentasulfide, phosphorus trisulfide, polysulfides, and the like. Each of these reagents gives somewhat different products, and by variations in the conditions of sulfurization, we may obtain two general types of products from each reagent regardless of sulfur content. One of these contains some active sulfur, and the other contains no active sulfur, that is, all the sulfur is in an inactive form. By active sulfur, we mean that form which is present when a 10 per cent blend of the sulfurized material with 90 per cent of gasoline, kerosene, or a lubricating oil (itself free from active sulfur according to this test) will appreciably discolor a bright copper strip immersed therein and held at 210° F. for 30 minutes. If the copper strip is not appreciably discolored, all the sulfur present is in an inactive form. If sulfur chloride or other sulfur halide is used for the sulfurizing reagent the final product may contain a halogen. The halogen may help activate the sulfur and is desirable for some purposes. If the combined action of sulfur and a halogen is desired and a sulfurizing agent is used which does not add halogen to the final product then the final product may be halogenated.

Both types of sulfurized products are useful for different purposes. For example, materials containing active sulfur are more effective components of gear lubricants and the like where extreme pressure is used and no easily corrodible metals are present. For crankcase use, however, especially where bearing metals sensitive to corrosion are employed, our product containing only inactive sulfur is preferred.

Various factors must be considered in the preparation of our sulfurized poly-isobutylene containing active and inactive sulfur. They are:

1. *Reagent.*—In general, for the preparation of sulfurized poly-isobutylene containing active sulfur, we prefer to use elemental sulfur combined with short times of heating and at lower temperatures. The sulfur compounds such as chlorides of sulfur and sulfides of phosphorus give products containing mostly inactive sulfur under sulfurizing conditions and are not so flexible with regard to variations in other conditions so sulfur itself, however, it is possible to use sulfur compounds to obtain products with active sulfur.

2. *Proportions of reactants.*—For the preparation of a product with active sulfur, we prefer to use large proportions of sulfur or sulfur compound because it is easier to obtain the desired product, other factors being constant. It is possible, however, at lower temperatures and with shorter periods of heating, to obtain active sulfur-containing products, using small amounts of sulfur. By controlling reagents and conditions, we are able to obtain sulfur-bearing derivatives with 2 to 20 per cent sulfur. For any given sulfur content, we may obtain a product containing only active sulfur.

3. *Temperature.*—Higher temperatures tend to fix the sulfur in inactive combination and are used when a stable sulfurized poly-isobutylene is desired. Use of lower temperatures with the same reagents and otherwise the same conditions gives a product containing active sulfur which is especially useful for cutting oils and extreme-pressure gear lubricants when blended with hydrocarbon oils and other ingredients.

4. *Time.*—We heat our reactants for a relatively short time to produce material with active sulfur and for a relatively long time to obtain only inactive sulfur in our product. Generally speaking, the length of heating time is inversely proportional to the temperature to which the product is heated.

5. *Solvents.*—Inert solvents may be employed, and they limit the highest temperature used in a particular sulfurization. If the solvent does not dissolve the sulfur or sulfur compound appreciably, the rate of reaction is slower and the formation of products containing active sulfur is favored. If the solvent dissolves the sulfur or sulfur compound, the reaction proceeds more rapidly and products containing only inactive sulfur are more readily obtained.

6. *Pressure.*—Under superatmospheric pressure, the sulfur is more stably fixed in the same time and under the otherwise same conditions. This is a useful modification of our process in order to obtain a product containing only inactive sulfur.

An example of the manufacture of our sulfurized poly-isobutylene suitable for use as an addition agent for lubricants is as follows: One hundred parts of tri-isobutylene are chemically combined with 10 to 15 parts of elemental sulfur, sulfur chloride, or phosphorus pentasulfide. This is accomplished by heating and stirring at temperatures from 280 to 340° F. Other amounts of sulfur and temperatures outside the given range may be used with somewhat different results. A short time of heating is sufficient when a product containing active sulfur is desired. Improved results are obtained by first mixing the tri-isobutylene with an equal volume of refined mineral oil before sulfurizing. The sulfurized product is not ready for use in a variety of lubricants such as gear lubricants, extreme-pressure lubricants, and cutting oils. It is merely blended with a suitable base oil in proportions of 0.05 to 20 per cent or more, depending on the amount of sulfur required in the lubricant. These blends yield far superior lubricants compared with the corresponding blends made from sulfurized fatty oils in that they contain no glycerine, either free or in combination. Glycerine compounds in a lubricant are prone to cause gumming and are less stable than the sulfurized product that is the addition agent of our invention. A further superiority of the latter is the relatively low viscosity of the blends at low temperatures as compared with the viscous blends that result when sulfurized fatty oils and the like are used. Another superiority of our sulfurized tri-isobutylene is that it is entirely free from any fatty acids, and therefore it is not corrosive in itself.

When the sulfurized poly-isobutylene is to be used as an inhibitor in a crankcase lubricant for protection of the new type bearings, it may be first refined to remove the H_2S or other impurities present. This may be done by blowing with inert gas or other suitable means. The sulfurized poly-isobutylene may be contacted with a selective solvent to remove any impurities formed during the sulfurization stage. Any sludge is allowed to settle thoroughly, and the product may be neutralized with fuller's earth or the equivalent, such as activated carbon, bauxite, lime, or caustic, at temperatures between 200° and 275° F. for several minutes. The mixture is filtered to remove the neutralizing agent. The finished product has a good color, and, when blended with a lubricating oil, does not affect the color or the emulsion test as do the sulfurized glycerides. Straight clay contacting may be used as the refining method.

The sulfurized poly-isobutylene prepared in a manner that produces an inactive sulfur compound does not affect the A. S. T. M. copper strip test of blends in lubricants when run for more than 30 minutes at 210° F. An addition of up to 2 per cent of this sulfur compound to a lubricating oil gives a lubricant which is practically free of any tendency to corrode the new type bearings, as determined by the Underwood corrosion test.

The manner in which this inhibitor stops corrosion is not known, but the following theory gives our version of what takes place, it being understood we base our invention on the improved results obtained and not on the theory. It is a fact that some metallic oxides and soaps have a strong catalytic effect on the oxidation of mineral oil, which in turn gives rise to the formation of corrosive organic compounds. Furthermore, it is known that the metallic sulfides are insoluble in mineral oil. It is assumed, therefore, that as soon as any metals, such as iron from the engine and copper, lead, or other metals from the bearings, start to corrode, they form the relatively inert sulfides instead of the active oxides and soaps, thus slowing down the rate of oxidation of the lubricant. A sulfur compound, to be a good inhibitor, must not be too stable or it cannot give up sulfur at a rate equal to the lubricant's tendency to form oxidation and soaps. Furthermore, it must not be too unstable or it will give up too much sulfur and cause corrosion from the action of free sulfur, which would first manifest itself in the darkening of copper parts. The sulfurized poly-isobutylene of our invention can be formed with the correct degree of stability.

The sulfurized poly-isobutylene described here-

in may be blended with any mineral, animal, synthetic, or vegetable oil to improve resistance to oxidation, with its attendant increase in sludge formation and tendency to corrode metals.

The action on blends in lubricating oils of our sulfurized poly-isobutylene may be enhanced by the presence of other compounds. Halogen and phosphorus compounds have an improving effect on the action of the sulfurized compound. For example, we may add to a blend of our sulfurized compound in a lubricating oil such compounds as chlorinated paraffin wax, chlorinated octadecanol, dichloropropyl ether, chlorobutyrone, octadecyl trichloroacetal, methyl dichlorostearate, chlorotolylstearamide, chloro-oleyl amine, chloro-oleyl amide, calcium dichlorostearate, barium derivative of tertiary amyl phenol sulfide, pentachlorodiphenyl, a chlorinated wax-naphthalene condensation product containing residual chlorine, trichlorophenol, trichlorodiphenyl ether, chlorodiphenylene oxide, chlorophenyl stearic acid, o-chloro-acetophenone, chlorobenzophenone, pentachlorophenyl benzoate, chlorobenzanilide, chlorophenyl phosphate, chlorophenyl phosphite, chlorophenyl phosphine, phosphazine, phosphanilide, phosphazo-benzene, phosphorus isothiocyanide, phosphoryl iso-thiocyanide, and the like. In general, any halogen or phosphorus-bearing organic compound having a vapor pressure of less than atmospheric at 140° C. has been found suitable as an auxiliary addition agent to our sulfurized poly-isobutylene.

It is to be understood that the examples hereinabove given are by way of illustration only and not by way of limitation and that the theories advanced with regard to the action of our sulfurized compound are our conception of what takes place. We do not wish to be bound by the theories but base our claims upon the improved results which are obtained.

Many modifications and variations of the invention as hereinabove set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claim.

Having thus described our invention, we claim:

A lubricant comprising in combination a major proportion of oil of lubricating viscosity and a minor proportion of the reaction product of a phosphorous polysulphide and tri-isobutylene, said reaction product having a negative A. S. T. M. copper strip test when run for at least 30 minutes at 210° F.

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