Patented June 6, 1944 2,350,959

UNITED STATES PATENT OFFICE

2,350,959

LUBRICATING OIL AND ADDITIVE THEREFOR

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No Drawing. Application October 17, 1942, Serial No. 462,416

11 Claims. (Cl. 252—33)

This invention relates to an improved lubricating oil and to a composition of matter particularly useful in improving the characteristics of lubricating oils when dissolved therein. More particularly the invention relates to the improvement of lubricating oils by the addition thereto of the reaction product of P_2S_5 and oil-soluble petroleum sulfonates.

It has become generally recognized that conventionally refined lubricating oils of either paraffinic or naphthenic base stocks are unable to fully meet the drastic requirements of heavy duty service such as required in internal combustion engines for trucks, busses, aeroplanes, tanks, marine engines, etc., which operate for long periods of time at high temperatures.

It has been found that under such extreme service conditions most conventional oils tend to decompose with undesirable results. For example, certain acidic products are formed in the oil through oxidation or decomposition which tend to attack and corrode alloy bearings. Other decomposition products tend to polymerize in the oil and form sludge which may interfere with the circulation of the oil through the lubricating system and may accumulate on the heated metal surfaces forming lacquer-like deposits. These deposits mixed with carbon from the incomplete combustion of the oil tend to collect in the piston ring slots affecting their free movement and causing either excessive consumption of oil or scoring of the cylinder walls of the engine.

Accordingly, the principal objects of the present invention are to provide a lubricating oil of the heavy duty type which is resistant to oxidation and sludge formation, non-corrosive to alloy bearings and other metal parts, and free from varnish formation and ring-sticking tendencies under the severe conditions of heavy duty service. These objects and others which will appear hereinafter are attained by us by providing a hydrocarbon lubricating oil containing the reaction product of P_2S_5 and an oil-soluble petroleum sulfonate. The preparation of this latter reaction product, which is a new composition of matter, will be described in greater detail hereinafter.

The addition of various chemical substances to lubricating oils to improve their resistance to oxidation and decomposition, to act as corrosion inhibitors, as sludge dispersants, as detergents, etc. has been proposed. While most of these compositions perform their intended function very well they do not correct all the difficulties encountered in heavy duty service. Certain of the compounds are added as detergents and disperse the sludge and prevent lacquer deposits and the sticking of piston rings. Unfortunately, however, many of these substances increase the rate of oxidation of the oil and their presence results in an increase in concentration of acidic oxidation products and an increased rate of corrosion of the bearings. Some substances added as anti-corrosion agents have no detergent properties and while they prevent corrosion they do not prevent sludge formation and varnish deposition on the engine parts. Adding detergents and anti-corrosion agents as separate compounds does not usually give satisfactory results.

Although the addition to lubricating oils of petroleum sulfonates has been suggested these compounds are not entirely satisfactory; their corroson inhibiting effect, particularly in certain types of oils, not being as good as desired. We have found, however, that if these petroleum sulfonates are heated with P_2S_5 a reaction occurs and the resulting product is much more efficient as an all-around lubricating oil additive to prevent corrosion, sludge formation, varnish deposition, etc.

The reaction between the petroleum sulfonate and P_2S_5 is conducted by us by merely mixing and heating the two substances at temperatures ranging from 90–110° C. until the reaction is substantially complete. This may be determined by observing the evolution of H_2S which is formed as a result of the reaction. Ordinarily after 2 to 4 hours heating substantially no more H_2S is given off and the reaction may be considered complete. Solvents such as toluene may be employed to reduce the viscosity of the reaction mixture and make it easier to handle. These solvents should be removed, however, before the product is added to the lubricating oil. This is best accomplished by evaporation under reduced pressure to remove the last traces of solvent.

The amount of P_2S_5 to be heated with the petroleum sulfonate may vary considerably since an excess of unreacted P_2S_5 is easily removed by filtration or decantation at the end of the reaction. On the other hand, small amounts of unreacted petroleum sulfonate in the product will not deleteriously affect its efficiency in lubricating oil. Accordingly, for each 100 parts by weight of petroleum sulfonate we may use from about 10 to 25 parts by weight of P_2S_5.

The petroleum sulfonates which we employ in the reaction to produce new lubricating oil additives are derived from the oil-soluble sulfonic

acids produced in the refining of petroleum products with sulfuric acid. The crude products usually contain mineral oil and because of their brownish-yellow color are frequently referred to as "mahogany soaps." It will be understood, of course, that the highly refined material may likewise be employed by us with satisfactory results. Although the structure of these sulfonic acids has not definitely been determined as yet it is generally believed that they have the formula $C_nH_{2n-12}SO_3$ and have a molecular weight ranging from about 300 to 600. Although the free sulfonic acids may be employed directly in the reaction we prefer to employ the metal salts thereof since in this form they are more conveniently handled and are more stable. Of the various metal salts of petroleum sulfonic acids, those of the alkaline earth group are preferred although salts of other metals such as Al, Sn, Zn, Mg, Na, Cd, Cu, Pb, Ni, etc., may be employed.

Since the structure of the petroleum sulfonates is not known it is obviously impossible to definitely give the structure of our new composition. It is certain, however, that the product contains phosphorus and sulfur resulting from a chemical reaction between the petroleum sulfonate and P_2S_5 in which H_2S is evolved.

The preparation of our new lube oil additives may be illustrated by the following examples in which the calcium salt of petroleum sulfonate was reacted with P_2S_5. It will be understood, however, that other salts of petroleum sulfonates may be employed in this reaction in different proportions from those specifically set forth. The example is given merely by way of illustration.

Example

400 parts by weight of a 65% solution of calcium petroleum sulfonate in mineral oil was dissolved in 150 parts by weight of toluene and stirred with 45 parts by weight of finely ground P_2S_5 at 95–105° C. for 3 hours. During this time H_2S was evolved and the mixture darkened somewhat. At the end of the reaction period the mixture was diluted with 150 parts by weight of toluene, cooled to room temperature and filtered from unreacted P_2S_5. 100 parts by weight of 97% alcohol was then added and the solution stirred with 30 parts by weight of finely ground calcium hydroxide at 35–40° C. until slightly alkaline to phenolphthalein indicator. The mixture was then filtered and about two-thirds of the solvent removed by evaporation under a gradually increasing vacuum.

Although products described in the preceding paragraph can be added directly to lubricating oils as such, or after complete removal of solvent, blending with the oil is facilitated by our practice of adding lubricating oil to the product as the solvent is being removed. The product prepared in this way is completely and almost instantly dissolved in conventional lubricating oils. Such a product was prepared by adding 120 parts by weight of a 10–W grade lubricating oil to the petroleum sulfonate-P_2S_5 reaction product described above, followed by evaporation of the remaining toluene and alcohol under a vacuum. The product thus obtained consisted of approximately 50% lubricating oil and 50% of the calcium salt of the petroleum sulfonate-P_2S_5 reaction product. The 50% oil solution was a yellowish-brown solution of medium viscosity.

A product prepared as thus described may be added directly to lubricating oils as a detergent, sludge dispersant and corrosion-inhibitor. Being highly effective it is necessary to employ only small amounts of the petroleum sulfonate-P_2S_5 reaction product to secure the desired effect. Ordinarily from 0.1 to 3.0% of the reaction product based on the total weight of the oil is sufficient. The petroleum sulfonate-P_2S_5 reaction product may constitute the sole additive in our lubricating oil or it may be used in conjunction with other materials added for special purposes. Alkyl phenol sulfides, such as salts of salicylic acid ester monosulfides, salts of acyl phenol sulfides, barium 2,4-diamyl phenyl monosulfide, etc. may for example, be added to the oil to increase the detergency and heat stability of the oil.

The effectiveness of a barium petroleum sulfonate-P_2S_5 reaction product, prepared by a process similar to that in the above example, as an anti-corrosion agent in lubricating oil may be demonstrated by the following results obtained by subjecting 30–W grade, Mid-Continent, solvent-refined lubrication oil to the Underwood Oxidation Test. In this test 1500 cc. of the oil was heated for 5 hours at 325° F. while continuously spraying portions of the oil against a 2'' x 10'' freshly sanded copper strip and a freshly sanded copper-lead allow strip with free circulation of air during the test. One sample of the oil served as a control, another sample contained 0.5% by weight of barium petroleum sulfonate. All of the samples contained 0.116% iron naphthenate, equivalent to 0.01% Fe_2O_3. At the end of the test the bearings were removed and weighed to determine their loss of weight by corrosion.

TABLE I

UNDERWOOD OXIDATION TEST

5 hours, 325° F.

	Bearing loss—mg.
Oil—control	104
Oil+0.5% barium petroleum sulfonate-P_2S_5 reaction product	11
Oil+0.5% barium petroleum sulfonate	136

These results show that the barium petroleum sulfonate-P_2S_5 reaction product is a much more effective corrosion inhibitor than the barium petroleum sulfonate alone. The neutralization number of the heated oils also showed that the barium petroleum sulfonate-P_2S_5 reaction product was very effective in keeping down the neutralization number of the heated oil, thus demonstrating its ability to prevent formation of corrosive acidic decomposition products in the oil under extreme service conditions.

The effectiveness of the barium petroleum sulfonate-P_2S_5 reaction product in reducing corrosion was also demonstrated by the standard Catalytic Indiana Oxidation Test. In this test 300 cc. samples of the oil containing 0.5% of the reaction product were poured into large glass test tubes and air bubbled through at the rate of 10 liters per hour while maintaining the tubes at a constant temperature of 341° F. Sanded strips of a copper-lead alloy were suspended in the oil and the bearing corrosion rates were determined by weighing the strips after 70 hours. Results of these tests were as follows:

TABLE II

CATALYTIC INDIANA OXIDATION TEST

Mid-Continent, 30–W grade, solvent-refined oil

	Bearing loss—mg.
Oil—control	275
Oil+0.5% barium petroleum sulfonate-P_2S_5 reaction product	+5 (gained)

The walls of the test tube containing the oil treated with the barium petroleum sulfonate-P_2S_5 reaction product were relatively clean after the test thus showing the detergent action of the additive. This test confirms the results of the previously described Underwood Test.

We claim:

1. A lubricating oil composition containing a major proportion of a lubricating oil and at least 0.1% by weight of the product obtained upon heating an oil-soluble petroleum sulfonate with P_2S_5 until the evolution of H_2S has substantially ceased.

2. A lubricating oil containing a major proportion of a hydrocarbon lubricating oil and 0.1 to 3.0% by weight of the product obtained upon heating an oil-soluble petroleum sulfonate with P_2S_5 at temperatures within the range 90–110° C.

3. A lubricating oil composition containing a major proportion of a hydrocarbon lubricating oil and 0.1 to 3.0% by weight of a compound prepared by heating 100 parts by weight of an oil-soluble petroleum sulfonate with 10 to 25 parts by weight of P_2S_5 at temperatures within the range 90–110° C. until the evolution of H_2S has substantially ceased.

4. A lubricating oil composition containing a major proportion of a hydrocarbon lubricating oil and 0.1 to 3.0% by weight of a compound prepared by heating 100 parts by weight of an oil-soluble petroleum sulfonate with 10 to 25 parts by weight of P_2S_5 at temperatures within the range 90–110° C. until the evolution of H_2S has substantially ceased and then neutralizing the product with an alkaline earth hydroxide.

5. A lubricating oil composition containing a major proportion of a lubricating oil and at least 0.1% by weight of the product obtained upon heating at temperatures within the range 90–110° C. an oil-soluble calcium petroleum sulfonate with P_2S_5 until the evolution of H_2S has substantially ceased.

6. A lubricating oil composition containing a major proportion of a lubricating oil and at least 0.1% by weight of the product obtained upon heating at temperatures within the range 90–110° C. an oil-soluble barium petroleum sulfonate with P_2S_5 until the evolution of H_2S has substantially ceased.

7. As a lubricating oil additive the composition of matter obtained upon heating an oil-soluble petroleum sulfonate with P_2S_5 until the evolution of H_2S has substantially ceased.

8. As a lubricating oil additive the composition of matter obtained upon heating an oil-soluble petroleum sulfonate with P_2S_5 at temperatures within the range 90–110° C.

9. As a lubricating oil additive the composition of matter obtained upon heating 100 parts by weight of an oil-soluble petroleum sulfonate with 10 to 25 parts by weight of P_2S_5 at temperatures within the range 90–110° C. until the evolution of H_2S has substantially ceased.

10. As a lubricating oil additive the composition of matter obtained upon heating at temperatures within the range 90–110° C. an oil-soluble calcium petroleum sulfonate with P_2S_5 until the evolution of H_2S has substantially ceased.

11. As a lubricating oil additive the composition of matter obtained upon heating at temperatures within the range 90–110° C. an oil-soluble barium petroleum sulfonate with P_2S_5 until the evolution of H_2S has substantially ceased.

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