United States Patent Office 3,595,820
Patented July 27, 1971

3,595,820

PROCESS FOR ENHANCING THE SULFUR RETENTION OF SULFURIZED POLYBUTENES

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No Drawing. Filed Oct. 14, 1968, Ser. No. 767,503
Int. Cl. C08f 47/00
U.S. Cl. 260—23 7 Claims

ABSTRACT OF THE DISCLOSURE

In a process for forming sulfurized polybutenes for use in metal working oils including reacting molten sulfur with low molecular weight polybutenes, stripping to remove light undesirable components such as hydrogen sulfide, various mercaptans and unreacted polybutenes, removing entrained sulfur and cooling to ambient conditions, the improvement which comprises enhancing the retention of chemically combined sulfur in such polybutenes by maintaining the pH in the range of about 2.0 to 5.5 for a period of time sufficient to substantially stabilize the chemically combined sulfur content of the sulfurized polybutenes. Suitably, the pH is maintained within the range set forth from after the stripping step until at least the ambient conditions are reached. Continued maintenance of the pH during storage is also desirable.

This invention relates to the sulfurization of olefins and, more particularly, to a process for sulfurizing polybutenes characterized by enhanced retention of sulfur.

Sulfurized addition agents in mineral lubricating oils have been extensively employed as metal working lubricants and as cutting oils. Such additives have also been widely used in extreme pressure applications. In such applications, it is theorized that the presence of sulfur allows the formation of metal sulfides on the working surfaces. These sulfided surfaces easily slide across one another to, in effect, provide increased lubricity. It is accordingly desirable to form a compound with as high a sulfur content as possible, consistent with color and other requisite properties of the oil, to minimize the amount of the sulfurized material that must be used to build up the sulfur content necessary to achieve the desired sulfided surfaces.

Particularly desirable as sulfurized addition agents are sulfurized polybutenes which are soluble in the low aromatic content mineral lubricating oils that are now being widely used. Desirably, these polybutenes have a sulfur content of about 12 to 20 weight percent, a minimum flash point, COC, of about 220° F., a maximum ASTM D–1500 color of about 8, and a gravity of about 18 to 28° API.

A minor proportion of such sulfurized polybutenes may be added directly to a major proportion of the low aromatic content oils. Alternatively, the sulfurized polybutenes may be reacted with about 0.5 to 1.5 parts, in volume proportions, of a liquid triglyceride such as lard oil and the reaction product then added to the mineral oils. Superior metal working lubricants having improved color characteristics are thereby formed.

To form these sulfurized polybutenes, an excess of elemental, molten sulfur is reacted at from about 250° F. to 400° F. with a liquid polybutene feed. The reaction product is then treated to remove light undesirable components such as hydrogen sulfide, various mercaptans, the unreacted polybutenes and entrained sulfur while bringing the product temperature down to ambient conditions. The sulfurized products, however, easily degrade, especially at higher temperatures, and extreme care must be taken in carrying out the steps set forth above.

Typically, the reaction product is first allowed to partially cool and is put down into a surge tank, with the residence time being anywhere from 3 to 16 or more hours. The lighter components, such as the unreacted polybutenes, may then be stripped with steam. Following this, the reaction product is cooled down to ambient conditions during which time the sulfur crystals are allowed to congeal to assist removal. The physical step of removal of the entrained sulfur may be carried out by filtering.

In performing these steps, it has been observed that up to 15 percent or more of the chemically combined sulfur may precipitate out from the sulfurized polybutene product. Since it is the sulfur content which is the measure of the yield, this sulfur loss creates a yield loss of 15 percent or more.

Potentially, this loss of sulfur may, of course, occur at any point after the reaction product has been formed. Modification of the temperatures and times utilized in the several steps involved in forming the final product will not however satisfactorily obviate the loss of chemically combined sulfur.

It is accordingly an object of the present invention to provide, in the sulfurization of polybutenes, a method for enhancing the retention of chemically combined sulfur in the sulfurized polybutene product.

Other objects and advantages of the invention will become apparent as the following description proceeds.

In accordance with the present invention there is provided, in a process for sulfurizing polybutenes which includes reacting an excess of elemental molten sulfur with a low molecular weight polybutene feed, stripping the lighter components such as hydrogen sulfide, various mercaptans and the unreacted polybutenes, removing the entrained sulfur and cooling to ambient conditions, the improvement comprising increasing the retention of chemically combined sulfur in the sulfurized polybutenes by maintaining the pH of the sulfurized polybutenes in a range from between about 2.0 to about 5.5 for a period of time sufficient to substantially stabilize the chemically combined sulfur content of the sulfurized polybutenes. It is preferred to continue to maintain the pH within the indicated range from after the stripping until at least the ambient conditions are reached. Significant advantages are achieved if the pH range is maintained even while the product is being stored for reasons which will hereinafter be developed.

Since, potentially, precipitation of sulfur could begin at any point after the reaction product has been formed, the maintenance of the pH at the desired level could be initiated anytime thereafter. Enhanced sulfur retention has been achieved by initiation of pH control after the lighter components have been removed.

While the pH may already be within the 2.0 to 5.5 range, the pH may be conveniently controlled by the addition of from about 0.005 to about 0.1 percent by weight of any organic carboxylic acid, alkyl sulfonic acid or alkyl or aryl acid phosphates that do not attack or otherwise adversely affect the sulfurized polybutenes being processed and are, of course, soluble in the polybutenes. To avoid any opportunity for the acid to adversely affect the stability of the reaction product, it is preferred to maintain the temperature below about 250° F. during and after the addition.

Representative examples of organic carboxylic acids which may be advantageously employed include hydrogenated dimer acid, acetic, chloroacetic, propionic, benzoic, octanoic, naphthoic, lauric, oleic and stearic. Suitable alkyl sulfonic acids are methane, ethane and propane.

Examples of alkyl and aryl acid phosphates include, respectively, dilauryl phosphate and diphenyl phosphate.

In accordance with one feature of the present invention, it is preferred to employ an acid which will not only maintain the pH within the range hereinbefore described but will also impart other desirable properties to the sulfurized product. For example, a hydrogenated dimer acid, i.e. a C_{36} aliphatic dibasic acid produced by polymerization of unsaturated C_{18} fatty acids and then hydrogenated, provides rust inhibiting properties. Other examples of acids which provide rust inhibiting properties include stearic and oleic acid.

Describing in more detail an exemplary process with which the present invention may be employed, a liquid polybutene feed of low molecular weight can be preheated to a temperature of from about 250° F. to 400° F. and charged to a batch reactor. The polybutene feed may be prepared by any conventional polymerization techniques designed to form low molecular weight products. While it is desirable to form polybutenes averaging from about 12 to 16 carbon atoms per molecule, a typical blend may well include molecules having from 4 to 20 carbon atoms.

An excess amount of sulfur, i.e. up to about 35 percent or more by weight, is charged in a molten state to the reactor and mixing is provided by stirrer. The reactor should be maintained between 250° F. and 400° F. Depending upon the temperature employed, the sulfurized polybutene product will be formed within a period of from about one to about 15 hours. The higher temperatures will diminish the time requirements.

The reaction product is then allowed to partially cool and is run into a surge tank where it is stored at from about 220° F. to 280° F. The storage time may extend from about 3 to about 16 hours, with shorter times being employed for higher temperatures. An acid addition to bring the pH to the desired level could be made at this point, if desired, especially if the surge tank temperatures are maintained in the lower part of the range.

Following completion of the storage in the surge tank, the reaction product is conventionally stripped with steam or an inert gas at temperatures in the range of 250 to 330° F. to remove the lighter components, i.e. hydrogen sulfide, various mercaptans and the unreacted polybutenes of lower molecular weight. It is at this point that sufficient acid is preferably added to the stripped sulfurized polybutene to maintain the pH between about 2 and about 5.5. Acid addition could, of course, be added before stripping takes place. In this event, the acid used should have a molecular weight sufficiently high to prevent its being stripped from the product with the other lighter components.

Conventionally, further processing of the sulfurized mixture may suitably involve further cooling, passing the cooled mixture thrugh a crystallizing operation to congeal any free sulfur that has been physically dispersed in the reaction mixture to facilitate removal and thereafter filtering the product at ambient conditions to remove any impurities such as the free sulfur. The filtered product may then be transported to a tank or other vessel for either storage or shipment. Although the sulfurized polybutenes are now relatively stable, the pH is preferably retained at the desired level during extended storage. Continued maintenance of the pH at the desired level will prevent sulfur loss that would otherwise occur if the product were to, for example, be passed through a line contaminated with a basic material such as an amine.

The following examples are intended to be merely illustrative of the present invention and not in limitation thereof. The determination of the acid number in the examples was carried out in accordance with ASTM–58.

EXAMPLE 1

A sulfurized polybutene ws made by preheating 600 gallons of a iquid polybutene feed containing a mixture of polybutenes having from 8 to 20 carbon atoms per molecular with carbon chains of 12 and 16 predominating. The average molecular weight was about 200. The feed was stripped from a higher boiling polymer obtained from the $AlCl_3$ catalyzed polymerization of butylenes. The preheated polybutene feed and 600 pounds of molten elemental sulfur was charged to a batch reactor equipped with stirrers.

The temperature of the reactor was maintained at about 350° F. After about one hour, the reaction product was removed from the reactor and steam stripped by throttling back 100 p.s.i.g. steam to maintain a steam temperature of about 300° F.

A one gallon sample was taken and separate samples were made by filling several 100 cc. glass beakers. The beakers were placed on hot plates and the temperature of the samples raised to about 240° F. Various materials were added to control the pH, the samples were allowed to cool and stand for a period of about 18 hours and data was obtained on the cooled supernatant liquid free from precipitated sulfur. The results are shown in Table 1:

TABLE 1

Additive	Wt. percent	pH	Sulfur, wt. percent	Total acid No.
None		2.9	14.4	1.61
Chloroacetic acid	0.02		14.8	5.7
Ethane sulfonic acid	0.03	2.8	14.8	3.7
"Ortholeum 162" (a principally dilauryl acid phosphate obtainable from E. I. du Pont de Nemours & Co.)	0.15	5.4	14.4	6.70
Plus "Primene 81 R" (C_{12}–C_{14} primary amines obtainable from the Rohm and Haas Co.)	0.05			
Reaction product of N-alkyl-1-3-propylenediamine and propylene carbonate (the alkyl group being a mixture of C_8 to C_{18})	0.20	6.0	12.3	0.60
"Primene 81 R"	0.05	7.0	12.9	1.49

EXAMPLE 2

Example 1 was repeated except other materials were added to control the pH. The results are shown in Table 2:

TABLE 2

Additive	Wt. percent	pH	Sulfur, wt. percent	Total acid No.
None		3.25	15.2	2.08
Hydrogenated dimer acid	0.05	3.95	15.4	2.12
"Primene 81 R"	0.03	6.25	13.4	1.24
Hydrogenated dimer acid	0.05	6.55	14.0	1.57
Plus "Primene 83 R"	0.03			

Thus, as has been seen, the present invention provides a method of enhancing the retention of chemically combined sulfur in sulfurized polybutenes. Maintaining the pH within the range indicated can prevent a sulfur loss of as much as 15% or more. In accordance with the preferred embodiment, the pH may be controlled by adding an acid that will also impart properties, such as rust inhibition, to the polybutene product.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof however, that is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the invention as expressed in the appended claims.

We claim as our invention:

1. A process for preventing the loss of sulfur from sulfurized polybutenes containing contaminants in amounts sufficient to raise the pH above a value of about

5.5 which comprises reacting an excess of molten sulfur with a low molecular weight polybutene feed to form a reaction product, stripping the reaction product to remove light components including hydrogen sulfide, removing entrained sulfur, cooling to ambient conditions and thereafter maintaining the pH of the reaction product in a range of from about 2.0 to about 5.5 by incorporating an additive selected from the group consisting of organic carboxylic acids, alkyl sulfonic acids, alkyl acid phosphates and aryl acid phosphates in at least the period following removal of the light components and until at least the ambient conditions are reached to enhance sulfur retention in the sulfurized polybutene reaction product.

2. The process of claim **1** wherein said additive is added in an amount of from about 0.005 to about 0.1 percent, based upon the weight of the reaction product.

3. The process of claim **2** wherein the temperature of the reaction product is maintained below about 250° F. during and after the acid addition.

4. The process of claim **2** wherein the acid added is hydrogenated dimer acid.

5. The process of claim **2** wherein the acid added is stearic acid.

6. The process of claim **2** wherein the acid added is oleic acid.

7. The process of claim **2** wherein the pH is maintained within said range during storage of the sulfurized polybutene reaction product.

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U.S. Cl. X.R.

252—45; 260—33.6, 45.7, 45.85, 79.5, 125, 139, 685