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THIOPHENE BY-PRODUCT TAR AND TRIGLYCERIDE OIL REACTION PRODUCT

Sigmund J. Lukasiewicz and Alexander N. Sachanen, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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This invention has to do with the development of improved lubricating compositions. More specifically, the present invention relates to the development of a novel class of characterizing agents which, when incorporated in hydrocarbon lubricating oils, inhibit the deleterious effects of oxidation upon the oils.

As is well known to those familiar with the art, various characterizing agents have been proposed for use in lubricants to counteract the chemical and physical shortcomings thereof. Among such shortcomings are, for example, tendencies to: oxidize, corrode metals with which they are in contact, form sludge and lacquer films on metal parts, deposit insoluble materials from acid bodies, etc. The present invention is concerned with overcoming some of these tendencies, notably with fortifying lubricants against the deleterious effects of oxidation and the formation of acid and sludge.

The present invention is based upon the discovery of a novel class of sulfur-containing reaction products which, when used in lubricating oils, effectively increase the resistance of said oils to oxidation. Thus, this invention is predicated upon the discovery that a new and novel class of reaction products, namely, sulfur-containing reaction products obtained by reaction of an animal, mineral, vegetable or essential oil, with a sulfur-containing tar obtained from a process for preparing thiophene and certain alkyl thiophenes, will so characterize lubricating oils.

The characterizing agents, as indicated above, are formed from an oil such as an animal, mineral, vegetable or essential oil. Typical of these oils which may be used herein are: animal—lard oil, sperm oil, etc.; mineral—paraffinic, naphthenic and aromatic oils or mixtures thereof; vegetable—rapeseed oil, soybean oil, cotton-seed oil, corn oil, palm oil, castor oil, oiticica; and essential—turpentine oil, lemon oil, peppermint oil, etc. Preferred of such oils are animal oils, of which lard oil is particularly preferred.

The sulfur-containing tars reacted herein with the aforesaid oils are obtained by reacting certain aliphatic hydrocarbons with sulfur as described at length in copending application Serial No. 601,758, filed June 27, 1945, by one of the present applicants, Alexander N. Sachanen, with H. E. Rasmussen and Rowland C. Hansford, now abandoned, and in copending application Serial No. 601,759, filed June 27, 1945, by said Rasmussen and Hansford, now issued as U. S. Patent No. 2,450,686. For convenience herein, however, the following is offered as a description of the process in which the tar is obtained as a by-product.

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Thiophene and a by-product tar are prepared by separately preheating sulfur and one or more normal aliphatic hydrocarbons selected from the group consisting of normal butane, normal butenes and butadienes to temperatures such that combining the sulfur and the hydrocarbon material will provide a mixture having a temperature in excess of about 450° C., mixing the preheated sulfur and preheated hydrocarbon, maintaining the temperature of the mixture at a temperature in excess of about 450° C. for a period of time of at least 0.01 second, and reducing the temperature of the mixture to less than about 450° C. Along with thiophene and the by-product tar, hydrogen sulfide and small amounts of carbon disulfide are also formed in the process. A sulfur-containing, by-product tar and alkyl derivatives of thiophene are also obtained by using an aliphatic hydrocarbon containing 5 or 6 carbon atoms and containing at least 4 carbon atoms in a chain, instead of a 4-carbon hydrocarbon in the foregoing process. Accordingly, the hydrocarbons used in preparing these tars are normal butane, normal butenes, butadienes, pentanes, pentenes, pentadienes, hexanes, hexenes and hexadienes, all having at least 4 carbon atoms in a chain, or mixtures thereof. It will be clear that a tar and thiophene are obtained from the aforesaid 4-carbon hydrocarbons; tars and alkyl derivatives of thiophene are obtained from the aforesaid 5 and 6 carbon hydrocarbons. As stated herein, and in the appended claims therefor, the term "sulfur-containing by-product tar" is used generically to describe those tars which are formed along with thiophene and those which are formed with alkyl derivatives thereof, such as the methyl and ethyl derivatives.

It has been found in the operation of this process that the relative proportions of sulfur and hydrocarbon material in the charge may be varied over wide limits. Too much sulfur, however, results in poor efficiency in sulfur utilization per pass, and favors the complete sulfurization of hydrocarbon material to carbon disulfied. Yet, too low a proportion of sulfur lowers the conversion per pass and the ultimate yield by increasing the overall thermal degradation of hydrocarbon material. Generally speaking, best results are obtained using a weight ratio of sulfur to a hydrocarbon material varying between about 0.5 and about 4.0; although when butenes, butadienes, pentenes, pentadienes, hexenes, or hexadienes constitute the bulk of the hydro-

carbon material in the charge, the lower limit of the weight ratio may be lower than 0.5. It should be observed however, that for economical operation of the process, it is preferred not to use a hydrocarbon charge consisting of butadienes, pentadienes, or hexadienes, because of their tendency to polymerize under the conditions of the process.

The selectivity of the reaction involved for the preparation of the tars and thiophenes depends, primarily, upon two variables, namely, reaction temperature at which the normal aliphatic hydrocarbon or hydrocarbons are contacted with sulfur and the reaction time or the time during which contact between the reactants is maintained at the reaction temperature.

The limits of operating temperature are fixed by the kinetics of the desired reaction and the kinetics of possible side or secondary reactions. It has been found, in this connection, that the reaction temperature may vary between about 450° C. and about 760° C. and preferably between about 540° C. and about 650° C. when normal butane is the predominant hydrocarbon reactant in the charge, and between about 480° C. and about 590° C. when butenes and butadienes are the predominant hydrocarbon reactants in the charge. With the 5 and 6 carbon hydrocarbons mentioned hereinabove, the reaction temperature may vary between about 450° C. and about 700° C. and preferably, between about 480° C. and between about 590° C. Below the lower limit of the temperature range (about 450° C.) the reaction is so slow as to require a large throughput of sulfur and a higher ratio of hydrocarbon recycle for a fixed amount of end product, therefore detracting from the economics of the operation. Above the upper limit of the temperature range which, as indicated hereinabove varies with the number of carbon atoms in the hydrocarbon reactant, the secondary reaction of degradation of hydrocarbon material in the charge takes precedence, therefore decreasing the yield of desired product. In addition to this, high temperatures favor the formation of carbon disulfide. It must be noted also that at these high temperatures corrosion problems are at a maximum, corrosion increasing perceptibly with increasing temperature.

It has been found, in connection with this process, that the optimum reaction time depends upon the temperature employed. In general, other variables remaining constant, the lower the temperature, the longer the reaction time. The reaction or contact time and the reaction temperature are somewhat fixed, one in relation to the other, between degree of degradation of the hydrocarbon material in the charge and between the extent or formation of undesirable products which may be tolerated. Thus, too long a contact time at high temperature results in severe cracking of the hydrocarbon material in the charge. The reaction proceeds with extreme speed, the only limitation apparently being the rapidity with which heat can be supplied to the reaction mixture. The reaction is highly endothermic requiring, by experimental measurement, approximately 28,000 calories per gram molecular weight of thiophene produced from normal butane. The lower limit of the range of reaction time is fixed, therefore, by the engineering problem of heat transfer and by mechanical limitations, such as allowable pressure drop across the reactor. Relatively long reaction times at temperatures in the neighborhood of the lower limit of the temperature range results in lower yields of thiophene and increased yields of thiophene tar. Too short a reaction time, however, at temperatures in the neighborhood of the lower limit of the temperature range results in insufficient reaction. Accordingly, it has been found that for best results the time of reaction is fixed by the reaction temperature.

In view of the foregoing, the criteria to be used in determining optimum operating temperatures within the range 450° C.–760° C. with 4 carbon hydrocarbons and 450° C.–700° C. for 5 and 6 carbon hydrocarbons and reaction times, are to chose the degree of conversion desired, commensurate with operating costs such as heat input and equipment costs, bearing in mind that within the limits, the shorter the reaction time, and correspondingly, the higher the temperature, the larger amount of end product which can be realized from a unit of given size per day.

It is recognized that the relationship between the temperature of reaction and reaction time is not singular with this process. It is a well established and fairly well understood relationship in numerous reactions. In this process, it has been found that a sulfur-containing, by-product tar and thiophene may be produced by reacting sulfur and the aforesaid 4 carbon hydrocarbons at a temperature between about 450° C. and about 760° C., and the tars and alkyl derivatives of thiophene may be produced by reacting sulfur and the aforesaid 5 and 6 carbon hydrocarbons at a temperature between about 450° C. and about 700° C., for a period of time selected to minimize the yields of secondary reaction products, such as carbon disulfide, coke-like materials, etc. at the selected temperature. Under such conditions, when operating continuously with the reactor coil of suitable size and at a particular charge rate, it has been found that the lowest practical limit of the time of reaction is of the order of 0.01 second at about 760° C. The upper practical limit of the reaction time, other variables remaining constant, will correspond to the lower limit of the temperature of reaction and may be of the order of several seconds.

Separate preheating of the hydrocarbon reactant and sulfur and quenching of the reaction mixture are necessary for achieving the relatively close control of the reaction time at a given reaction temperature. This is very important in the specific reaction producing thiophene and tars. It is suspected that a number of reactions occur in the reaction between the hydrocarbon reactant and sulfur. In this connection the following should be noted: cracking of the hydrocarbon reactant destroying the 4 carbon atom chain structure (prerequisite for the formation of thiophene and alkyl derivatives thereof); formation of tars high in sulfur; and formation of carbon disulfide. These reactions compete with one another. It has been found that the rates of the formation of lighter hydrocarbons and of the formation of carbon disulfide are somewhat slower than those required for the formation of thiophene and tars. Accordingly, a proper control of the reaction time at a given reaction temperature achieved by separate preheating, mixing, heating at a given temperature for an increasing period of time and quenching is necessary to produce high yields of thiophene and tars with limited yields of carbon disulfide, coke-like materials, and fixed gases due to a limited decomposition of the hydrocarbon reactant. The rate of the reaction producing tars

is fairly close to that required for the formation of thiophene and the yields of tars and of thiophenes are approximately the same.

In carrying out the process for preparing tars, it is essential to separately preheat the reactants. Heating the hydrocarbon material and sulfur together is undesirable, in that heavy tars are produced and these are subsequently cracked in the reactor causing undue coke formation. Tests have shown that when the reactants are heated together, up to temperatures within the aforementioned reaction temperature ranges, tar formation is favored as is subsequent cracking thereof with the result that the reaction zone is eventually filled with a heavy, carbonaceous deposit. Therefore, it is essential to separately preheat each of the reactants, i. e., the hydrocarbon or mixtures of hydrocarbons and sulfur to such temperatures that when they are brought together, under proper conditions of flow, a temperature falling within the reaction temperature range is achieved before effecting contact between them. In practice, this is effected ordinarily by separately preheating each of the reactants to temperatures within the reaction temperature range.

After the separately preheated hydrocarbon reactant and sulfur are mixed and allowed to react for the reaction time indicated by the operating temperature, the temperatures of the reaction mixture are immediately lowered to below about 450° C., in practice, appreciably below 450° C. in order to avoid over reaction in the system after leaving the reactor. This may be achieved suitably by spraying the effluent of the reactor with a liquid. In preparing the tars, reaction is effected preferably at atmospheric pressure or sufficient pressure caused to flow the reactants through the reactor and auxiliary system under the desired reaction conditions. Tests have shown that the yield per pass and ultimate yield of thiophene decreases with increase in pressure. However, even at appreciable pressures, thiophene and tars are nevertheless produced in substantial amounts. Accordingly, there appears to be nothing critical about pressure as a reaction variable. It has been found that the best results are obtained when turbulent flow is maintained through the reactor, suitably a conventional coil-type pipe reactor. With this type of reactor, the desired turbulent flow may be achieved with a pressure drop of about 1–20 pounds across the coil, depending upon the size of the pipe and the length of the coil. Turbulent flow promotes heat transfer and assures good testing of the reacting variables of sulfur and hydrocarbon reactants.

The following detailed example is for the purpose of illustrating the production of thiophene and tar, in accordance with the foregoing process.

EXAMPLE I

Preparation of sulfur-containing by-product tar

Normal butane was charged into a preheater at the rate of 39 grams per minute and heated to a temperature of 645° C. Sulfur was charged to a separate preheater at a rate of 145 grams per minute and heated to a temperature of 645° C. The two streams were sent through a mixing nozzle and thence through a baffled tube reactor of 200 cc. volume constructed of 27 per cent chromium, stainless steel maintained at a temperature of 665° C. The reaction product was quenched with a water spray passed through a small Cottrell precipitator to remove tar mist and scrubbed through a hot countercurrent caustic tower. Liquid product was condensed and separated in a water cooler and ice trap. The residual gas was metered. Of the hydrocarbon material charged, 60 per cent was converted to light product and tar, in approximately equal amounts. Fractionation of a portion of the stabilized (i. e., after removal of C_4 hydrocarbon and lighter constituents) light product showed the following composition:

	Per cent
Carbon disulfide	27.3
Thiophene	70.3
Residue (mostly thiophene)	2.4

The tar thus obtained was a dark, viscous mass having the following characteristics:

Composition:

Carbon	25 per cent
Hydrogen	1.8 per cent
Sulfur	73.0 per cent

Properties:

Molecular weight (average)	317
Specific gravity	1.5066 at $\left(\frac{82°F.}{60}\right)$
Pour point	—15° F.
S. U. V.	46 seconds at 210° F.

The tar described in Example I above is illustrative of the tars reacted herein with an oil of the type described above. The tar is substantially soluble in benzene and in aqueous alkaline solutions indicating the acidic nature of its constituents. It has been found, however, that the composition of the tars varies with the aliphatic hydrocarbon from which they are prepared and varies as well with the conditions under which they are prepared. As such, it is not possible at this time to ascribe any representative formula or formulae to the tars, and they can be more accurately defined, therefore, as reaction products in terms of the reactants from which they are derived and the reaction conditions under which they are derived.

The reaction products contemplated herein are illustrated in the following example:

EXAMPLE II

Preparation of lard oil-tar (Example I) reaction product

Lard oil (280 grams) and the tar of Example I (57 grams) were heated together at approximately 180° C. for a period of 4 hours and 45 minutes. During this time the reaction mixture was continuously agitated and during the greater part of this period, hydrogen sulfide was evolved which is indicative of reaction taking place between the reactants. The reaction product was cooled and filtered through Super Filtrol. The filtrate was a dark-colored liquid containing 11.8 per cent of sulfur (product I).

The reaction product was tested in order to determine its corrosive or non-corrosive nature in the following manner. One per cent by weight of the reaction product was blended in neutral mineral oil (S. U. V. 53 seconds at 210° F.) and a bright copper strip was immersed in the resulting blend. After 24 hours at 100° C. the copper strip was only slightly stained. A second, one per cent blend of the reaction product in a highly aromatic fraction (boiling range 91° C. to 141° C.) was agitated with a small amount of metallic mercury for 3 minutes. The mercury was not tarnished by this treatment. Accordingly, the

reaction product is substantially non-corrosive.

The foregoing example of a typical reaction product is but illustrative, inasmuch as the reaction temperatures used in preparing the same may be varied considerably. For example, temperatures of the order of 160° C. to about 250° C. are generally used, with preference being given to those within the range from about 180° C. to about 200° C. Similarly, the reaction time may be varied and depends, to a large degree, upon the quantities of materials which are reacted together and upon the reaction temperatures used. In general, longer reaction times should be used, all other conditions being constant, with lower temperatures of the aforesaid temperature ranges; correspondingly, shorter reaction times may be used with temperatures at the upper end of the aforesaid temperature ranges. As a guide to preparing sulfur-containing reaction products of the aforesaid type, it is preferred that the reaction be carried out for a sufficient period of time, in order that the reaction product thus obtained be substantially non-corrosive. This characteristic may be determined as indicated above in Example II, wherein the corrosive nature of hydrocarbon blends of the reaction product were tested with a copper strip and with metallic mercury. A reaction product is considered substantially non-corrosive when the copper strip is not discolored or is only slightly stained, or when the mercury in contact therewith is not tarnished.

Considerable variation also obtains in regard to the relative proportions of oil and tar reactants. The sulfur content of the reaction product may be controlled, by varying the proportions of lard oil and tar. Increasing the ratio of lard oil decreases the sulfur content and increasing the ratio of tar increases the sulfur content. Thus, if a sulfur content of 10–12 per cent is desired, the relative proportions are: 1 part of tar by weight to 5 parts of lard oil.

To demonstrate the effectiveness of the reaction products of this invention as oil-improving agents, lubricating oil blends containing typical reaction products were subjected to the tests described below:

CORROSION TEST

A section of a bearing containing a cadmium-silver, alloy surface and weighing about 6.0 grams, was placed in a solvent-refined Pennsylvania oil of S. U. V. of 53 seconds at 210° F. The oil was heated to 175° C. for 22 hours while a stream of air was bubbled against the surface of the bearing. The loss in weight, in mgms., of the bearing is indicative of the corrosiveness of the oil. In each case a sample of the oil containing the characterizing agent was run concurrently with a sample of straight or uninhibited oil. Each sample contained a section cut from the same bearing. The results are set forth in Table I below:

Table I

Improving Agent	Conc. (Weight Per Cent)	Loss in Weight (Mgms.)	
		Inhibited Oil	Uninhibited Oil
Product I	0.25	1	25
Do	0.5	0	25
Do	1.0	0	25

OPERATION TEST

The oil employed in this test was a solvent-refined oil having a S. U. V. of 45 seconds at 210° F. and the test procedure involves the following: The tests were carried out in a single cylinder lauson engine operated continuously over a time interval of 36 hours with a cooling medium held at a temperature of about 212° F. and the oil temperature held at about 280° F. The engine was operated at a speed of about 1830 R. P. M. At the end of the test, the oil was tested for acidity (in terms of the Neutralization Number or N. N.) and viscosity. The results of these tests are tabulated in Table II below.

Table II

Improving Agent	Conc. (Weight Per Cent)	N. N.	K. V. @ 210° F.
None		13.6	11.36
Product I	1.0	7.0	8.39
None		9.3	7.72
Product I	2.0	0.8	5.92

It will be apparent from the foregoing test data that the reaction products contemplated herein are effective corrosion and oxidation inhibitors. When incorporated in oil, these reaction products may be used in relatively small amounts, depending upon the intended purpose and upon the oil with which they are used. When used as corrosion and oxidation inhibitors, concentrations from about 1 per cent to about 3 per cent are generally satisfactory, with concentrations of the order of 2 per cent being preferred. They may also be used in cutting oils or as cutting oils per se. Cutting oils, however, may contain substantially larger amounts such as of the order of 10–20 per cent.

These reaction products may also be used as rubber accelerators. Numerous other uses and applications will be readily apparent to those skilled in the art from the foregoing discussion of the composition of these reaction products and from the typical procedures for preparing them.

It is to be understood that although certain preferred reaction products and certain preferred procedures for preparing the reaction products contemplated herein have been illustrated hereinabove, the invention is not limited to the said products or procedures, but includes within its scope such changes and modifications as fairly come within the spirit of the appended claims.

This application is a division of an application, Serial No. 654,222, filed March 13, 1946, now matured into U. S. Patent No. 2,480,660, issued August 30, 1949.

We claim:

1. As a new composition of matter, a sulfur-containing reaction product obtained by reacting about 5 parts by weight of a triglyceride oil with about 1 part by weight of a sulfur-containing by-product tar, at a temperature of from about 160° C. to about 250° C., said tar being obtained by: separately preheating sulfur and a hydrocarbon selected from the group consisting of normal butane, normal butenes, butadienes, pentanes, pentenes, pentadienes, hexanes, hexenes and hexadienes, said hydrocarbon having at least four carbon atoms in a straight chain, to temperatures such that combining said sulfur and said hydrocarbon will provide a reaction mixture having a temperature varying between 450° C. and about 760° C. when the said hydrocarbon is one of the aforesaid four-carbon hydrocarbons, and between 450° C. and about 700° C. when the said hydrocarbon is one of the aforesaid five- and

six-carbon hydrocarbons; mixing the preheated sulfur and the preheated hydrocarbon in a weight ratio of sulfur to hydrocarbon varying between about 0.5 and about 4.0; reacting said preheated sulfur with said preheated hydrocarbon at a reaction temperature varying between 450° C. and about 760° C. when the said hydrocarbon is one of the aforesaid four-carbon hydrocarbons, and between 450° C. and about 700° C. when the said hydrocarbon is one of the aforesaid five- and six-carbon hydrocarbons, for a contact time of from about 0.01 second to several seconds, to produce a reaction mixture containing thiophene and a sulfur-containing tar; reducing the temperature of said reaction mixture to less than 450° C.; and separating said tar from said mixture.

2. As a new composition of matter, a sulfur-containing reaction product obtained by reacting about 5 parts by weight of lard oil with about 1 part by weight of sulfur-containing by-product tar, at a temperature of from about 160° C. to about 250° C., said tar being obtained by: separately preheating sulfur and a hydrocarbon selected from the group consisting of normal butane, normal butenes, butadienes, pentanes, pentenes, pentadienes, hexanes, hexenes and hexadienes, said hydrocarbon having at least four carbon atoms in a straight chain, to temperatures such that combining said sulfur and said hydrocarbon will provide a reaction mixture having a temperature varying between 450° C. and about 760° C. when the said hydrocarbon is one of the aforesaid four-carbon hydrocarbons, and between 450° C. and about 700° C. when the said hydrocarbon is one of the aforesaid five- and six-carbon hydrocarbons; mixing the preheated sulfur and the preheated hydrocarbon in a weight ratio of sulfur to hydrocarbon varying between about 0.5 and about 4.0; reacting said preheated sulfur with said preheated hydrocarbon at a reaction temperature varying between 450° C. and about 760° C. when the said hydrocarbon is one of the aforesaid four-carbon hydrocarbons and between 450° C. and about 700° C. when the said hydrocarbon is one of the aforesaid five- and six-carbon hydrocarbons, for a contact time of from about 0.01 second to several seconds, to produce a reaction mixture containing thiophene and a sulfur-containing tar; reducing the temperature of said reaction mixture to less than 450° C.; and separating said tar from said mixture.

3. As a new composition of matter, a sulfur-containing reaction product obtained by reacting about 5 parts by weight of lard oil with about 1 part by weight of a sulfur-containing by-product tar, at a temperature of from about 160° C. to about 250° C., said tar being obtained by: separately preheating sulfur and normal butane to temperatures such that combining said sulfur and normal butane will provide a reaction mixture having a temperature varying between 450° C. and about 760° C., mixing the preheated sulfur and the preheated normal butane in a weight ratio of sulfur to butane varying between about 0.5 and about 4.0; reacting said preheated sulfur and said preheated normal butane at a temperature falling between 450° C. and about 760° C. for a contact time of from about 0.01 second to several seconds to produce a reaction mixture containing thiophene and a sulfur-containing tar; reducing the temperature of said reaction mixture to less than 450° C., and separating said tar from said mixture.

SIGMUND J. LUKASIEWICZ.
ALEXANDER N. SACHANEN.

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