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SULPHURIZED HYDROCARBON AND METHOD OF PREPARATION

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This invention relates to a sulphur-containing hydrocarbon, and more particularly to a sulphur derivative of an aliphatic hydrocarbon, to a process for manufacturing this product, and to a process of modifying lubricating oils with this product.

In the progressive development of lubricants it has been found that specific qualities and general utility of hydrocarbon oils can be improved by incorporating small amounts of various materials, commonly generalized as "additives." An additive may serve to improve the quality of a lubricant in any one or more of several ways, for example, by decreasing the rate of oxidation, increasing the film strength, increasing the dispersing power of an oil for insolubles, and so forth. At times it may be desirable to use more than one additive in an oil in order to impart properties making it most suitable for some specific application. A wide variety of compounds and mixtures has been disclosed in the field of lubricant additives.

Most lubricating oils can be improved by adding small amounts of selected oxidation inhibitors. These inhibitors are particularly effective in synthetic oils and in oils which have been subjected to intensive refining processes. The natural lubricants contain small amounts of materials that act as oxidation inhibitors, but these are largely removed by many refining treatments, particularly solvent extraction treatments. In most cases the highly refined lubricants produced at the present time are inferior in resistance to oxidation to the lubricants produced by the previously conventional methods, such as acid and clay treating, although they may be superior in other respects, such as viscosity index. The addition of inhibitors to these oils is necessary to impart stability for satisfactory engine lubrication.

The synthetic lubricants, such as those produced by the hydrogenation of olefin polymers, may be particularly susceptible to oxidation as compared to natural lubricants. In these cases, also, high resistance to oxidation can be imparted to the oil by adding selected oxidation inhibitors.

The development of oxidation inhibitors for oils is therefore of great importance, but is complicated by the severe requirements that the inhibitor itself must meet. Any material added to an oil to improve one property should not adversely affect any other property. The inhibitor itself should not be corrosive to engine parts. The concentration in the oil should not decrease rapidly during use either from loss by volatilization, from preferential decomposition by the action of heat, from excessive reaction with engine parts, or from other causes. The inhibitor should not impart an undesirable color or odor to the oil, or in any other manner adversely affect the utility or performance of the oil.

Many attempts have been made to develop additives that improve more than one specific quality of an oil; the advantages of this type of additive are readily appreciated. For example, certain additives have been claimed to both increase film strength and inhibit oxidation, others have been claimed to decrease the pour point and increase film strength, and still other combinations of properties have been claimed for specific additives.

Sulphur or compounds containing sulphur have been used in cutting oils and oils used in other applications where high pressures are developed between the moving metal surfaces. More recently this type of lubricant has been extensively used in the hypoid gears of automobile differentials. These lubricants are known as "extreme pressure" lubricants because the film of lubricant must withstand the high pressures existing at the points of gear contact. In these applications, it is important that the activity of the sulphur be so controlled as to eliminate seizure and scuffing or tearing of the metal surfaces, but must be sufficiently resistant to change to introduce no objectionable characteristics.

More recently, organic materials containing sulphur have been used as additives for crankcase lubricating oils. For crankcase lubrication, high film strength is not a critical property, but if high film strength can be obtained without sacrificing other properties, it is very desirable, because such an oil will minimize engine failures caused by seizure of close-fitting parts, particularly during the break-in period, and may decrease general maintenance requirements of the engine. The most important function of sulphurized compounds in crankcase oils is the inhibition of oxidation. The effect of oil oxidation has been briefly summarized hereinbefore, and the importance of oxidation control pointed out. Certain types of sulphurized compounds have proven effective for diminishing the rate of oxidation of oils. It has appeared that this inhibition of oxidation results primarily from a deactivation of the metal catalysts found in an engine, especially iron and iron salts.

One general group of sulphurized materials have prepared by reacting unsaturated organic compounds with sulphur or active sulphur compounds such as sulphur chloride, for example.

Various natural oils have been used as the unsaturated charge, but these oils usually contain a wide variety of organic materials having several points of reactivity, so that the resultant sulphurized oil is a heterogeneous mixture of sulphur compounds.

It is an object of this invention to provide an improved material for use as a lubricant additive.

Another object of this invention is to provide a sulphurized hydrocarbon of uniform composition.

Another object of this invention is to provide a material consisting of carbon, hydrogen and sulphur which when added to a lubricant will increase the film strength and decrease the rate of oxidation.

Another object of this invention is to produce sulphurized hydrocarbons of high molecular weight, which are superior lubricant additives, from ethylene as the initial hydrocarbon source.

Another object of this invention is to provide a sulphurized hydrocarbon to be used as a lubricant additive in which the position of the sulphur in the molecule is controlled.

Another object of this invention is to provide a sulphurized hydrocarbon to be used as a lubricant additive in which the activity of the sulphur is controlled.

Another object of this invention is to provide a light-colored uniform type of organic sulphur compound to be used as a lubricant additive.

Still another object of this invention is to prepare a relatively stable sulphur-containing hydrocarbon in which the reactivity of the sulphur is carefully adjusted and uniformly controlled.

Another object of this invention is to disclose a sulphur derivative of an aliphatic hydrocarbon, in which the activity of the sulphur is uniformly adjusted to the proper value for specific applications.

Other objects will be evident to one skilled in the art from the accompanying description and discussion.

The olefin hydrocarbons used in the embodiment of my invention are prepared by polymerizing low molecular weight mono-olefins, preferably ethylene or mixtures containing ethylene, using as catalyst an oxide of an iron group metal, such as nickel oxide prepared as hereinafter disclosed, which is effective in polymerizing olefin hydrocarbons. Such a catalyst may be prepared from an active nickel-on-kieselguhr hydrogenation catalyst, by heating the catalyst to a temperature above about 450° C., but not above about 700° C., and passing over the catalyst a stream of inert gas containing a small percentage of oxygen, for example a mixture of nitrogen and oxygen containing about 2 to 10 per cent oxygen, until substantially all of the nickel has been converted to oxide. The oxidation is preferably so conducted that a uniform temperature prevails throughout the catalyst mass, and that uniform oxidation is obtained. One means of achieving this is to agitate the catalyst during the oxidation process.

The mono-olefin-containing charge is polymerized by contacting it with the catalyst at a temperature in the range of about 50 to 200° C. and a pressure in excess of atmospheric, usually in the range of 400 to 1500 p. s. i. Ethylene is the preferred olefinic charge, since polymers of higher molecular weight and more limited chain branching result from it than from other reactive olefins.

The catalyst for this polymerization is very sensitive to certain poisons, such as sulphur, ammonia, carbon monoxide, certain organic compounds containing oxygen, sulphur or halogens and other materials the exact nature of which is not known. It is therefore necessary that the charge be very carefully freed from all such material before contacting with the catalyst. Commercial olefins, such as ethylene, of high purity may advantageously be further purified by passage over reduced nickel-on-kieselguhr hydrogenation catalyst at about 175° C. and then through sodium hydrate adsorbent at room temperature. Further improvement in catalyst life has been obtained by operating the catalyst in the presence of an alkali metal, alloy, or amalgam of alkali metals, preferably in the liquid state. It is believed that these added metals act to remove traces of materials introduced into or formed in the reaction system that adversely affect the activity of the catalyst.

The products obtained by the polymerization of ethylene range from butenes to high melting point waxy hydrocarbons. A fraction containing olefins of 16, or more, carbon atoms per molecule is separated for use as sulphurization charge stocks. For example, the low boiling olefins are removed by distillation, leaving a residue boiling above about 300° C. This residue is a colorless semi-solid waxy olefin containing one double bond per molecule. All of this residue may be used, or some fraction thereof of narrow-boiling range.

The olefinic products of this polymerization system have been found to contain no tertiary-base olefins, and substantially no chain-branching, as indicated by their waxy nature or high melting point. There are no cyclic or aromatic hydrocarbons in the product. It is thus apparent that ethylene is converted to polymeric products in this catalytic system by simple polymerization without isomerization, hydrogenation, or other changes. The double bond is at or near the terminal position in the olefin molecules, and I believe that the favorable results realized are obtained because I am able to produce normal olefins of 16 or more carbon atoms per molecule and to produce sulphurized products therefrom. The polymeric products from propylene and higher boiling olefins are less desirable in that the polymers are lower in molecular weight, and greatly increased numbers of side-chains are found in the polymers.

The uniformity of molecular structures and characteristics of these polymers from nickel oxide catalyzed polymerizations makes them well suited for conversion with sulphur to sulphurized products of uniform activity without further segregation or purification. In addition, through control of the proportion of sulphur combined with the olefin, the activity of the sulphur compounds may be controlled within relatively narrow limits.

The polymers produced from ethylene by means of the nickel oxide or similar catalyst thus differ in significant properties from the polymers produced in the presence of acid, metal halide, or clay-type catalysts; the latter polymers contain generally tertiary-base olefins, extensive chain branching, internal unsaturation, and so forth, and frequently undergo isomerization, cyclization and other secondary changes during processing.

Sulphur may be introduced into polymer fractions in the desired molecular weight range by reaction with sulphur, sulphur chloride, hydrogen sulphide, or other suitable sulphur-contain-

ing compounds; however, these means of introducing sulphur are not equivalent. A preferred type of reaction product results from the heating of about two to fifteen parts by weight of sulphur with 100 parts of olefinic hydrocarbon at a temperature in the range of from 180 to 280° C. for a period of about 1 to 10 hours. The proportion of sulphur used depends on the molecular weight of the polymer and the desired activity of the product. In general, the proportion of sulphur used is in the range of 0.4 to 2.0 atoms of sulphur per molecule of olefins, although in some applications higher proportions of sulphur may be desirable. The reactivity of the resulting sulphur compounds increases with increase in sulphur content of each molecule of the reaction product.

It is usually necessary that the sulphur be completely combined with the hydrocarbon, so that no highly corrosive elementary sulphur remains in the mixture. In some cases, especially with the lower proportions of sulphur, the reaction can be completed by heating the reactants in the preferred temperature range of 210 to 240° C. During the reaction, the solution gradually changes in color from a light yellow imparted by the dissolved sulphur to the reddish orange color of the sulphur-containing products. No gas is evolved, and no black or insoluble compounds are formed during the reaction.

In some cases the reaction of sulphur with the very pure olefin proceeds at a very low rate. Small amounts of various materials may be added to the reaction mixture to accelerate the reaction, to aid completion of the reaction, and to permit the formation of the product to be conducted at a lower temperature. Suitable catalysts, which may be used in concentration of about 0.01 to 0.2 per cent or more, are halogens, especially iodine, and some nitrogen compounds such as high boiling amines. These catalysts are usually employed in such low concentrations that their presence in the product is often not important. They may be removed by chemical means when desired.

The sulphur-containing compound is sufficiently light in color that it may be blended with lubricating oils in concentrations as high as 10 or 15 per cent without important effect on the color of the oil. In highly refined oils, the beneficial effect of as little as 0.05 per cent of the sulphurized hydrocarbon may be appreciable; usually from 1 to 5 per cent of the sulphurized hydrocarbon is added to lubricating oils, so that the sulphur content of the oil is increased by 0.05 to 0.20 per cent or thereabouts. In cutting oils, gear lubricants, and the like, the sulphur-containing hydrocarbon may be used in concentrations as high as 20 per cent or more.

The following examples describe specific preparations of sulphurized hydrocarbons, in accordance with my invention.

Example I

One hundred parts by weight of a pelleted, active, reduced nickel-on-kieselguhr hydrogenation catalyst containing 55 per cent nickel was placed in a glass tube and heated in an electric furnace to 550° C. A mixture of two per cent oxygen in nitrogen was passed over the catalyst at such a rate that the theoretical amount of oxygen to convert the nickel to nickel oxide had been introduced at the end of four hours. The catalyst was continuously agitated during this period and the furnace held at the initial temperature. The catalyst was cooled and transferred to a pressure autoclave containing one and one half parts by weight purified normal pentane and one-twentieth part of metallic sodium. The autoclave was assembled and heated to 110° C., and purified ethylene was introduced to a total pressure of 600 pounds per square inch gauge. As the polymerization proceeded, more ethylene was added to maintain the pressure at the original figure. The autoclave was continuously shaken, and the temperature was held at 110–115° C. Two hundred parts by weight of ethylene were polymerized during a 5 hour period.

The reaction was discontinued, and the product was removed from the reactor. The product boiling below 300° C. was removed by distillation, leaving a colorless semi-solid waxy residue.

Ten parts by weight of this residue was mixed with 10 parts of paraffinic oil and one part of sulphur. The mixture was stirred and heated to 220° C. for six hours. During this period the color deepened from a light yellow to a reddish orange as the sulphur reacted with the olefin. No evolution of hydrogen sulphide was detected. At the end of the stated time the reaction was complete, as indicated by the absence of elementary (corrosive) sulphur.

A highly refined lubricating oil was used in a four-cycle engine operating under severe conditions for 50 hours; the test was repeated using another portion of the highly refined oil to which 4 per cent of the sulphurized oil previously described was added. The difference in oxidation of the oils is evident from the following data on the acid content and viscosity increase of the two oils.

	Highly refined oil	Highly refined oil plus 4 percent sulphurized oil
Neutralization number	5.2	0.8
Increase in viscosity, percent	7.6	2.3

Example II

From the polymer product prepared from ethylene as in Example I the portion boiling above 240° C. was segregated. To fifty parts by weight of the olefinic polymer was added ten parts of sulphur and 0.02 parts iodine. This mixture was heated at 210° C. for three hours; after this treatment the sulphur was found to be chemically combined with the oil. This mixture was then diluted with paraffin oil and used as a cutting oil mixture.

These examples are included to exemplify specific embodiments of my process, and should in no way be considered to limit unnecessarily the scope of this invention. Many modifications can be applied by those skilled in the art without departing from the spirit of the disclosure or scope of the claims.

I claim:

1. A sulphur-containing aliphatic hydrocarbon prepared by polymerizing ethylene in the presence of an oxide of a metal of the iron group, segregating a polymer fraction boiling above 240° C. from the total product, and reacting said polymer fraction wth a sulphurizing agent to form a sulphurized hydrocarbon.

2. The process of preparing a sulphurized hydrocarbon material, which comprises subjecting ethylene to the action of an oxide of a metal of the iron group as a polymerization catalyst under such conditions that the ethylene is polymerized

to substantially entirely straight-chain polymers, separating from effluents of said polymerization a polymer fraction comprising polymers of at least 16 carbon atoms per molecule, and chemically combining said polymer fraction with about 0.4 to 2 atoms of elementary sulphur per molecule of polymer material to produce a sulphurized hydrocarbon.

3. The process of claim 2 in which said polymer fraction is freed from compounds boiling below the lubricating-oil range prior to said combining with sulphur.

4. The process of claim 2 in which said polymerization catalyst comprises oxidized nickel.

5. The process of claim 2 in which said polymerization catalyst is prepared by subjecting an active nickel-on-kieselguhr hydrogenation catalyst to the oxidizing action of a gaseous atmosphere containing about 2 to 10 per cent free oxygen, the remainder of the atmosphere being inert to said hydrogenation catalyst, until substantially all of the nickel has been converted to nickel oxide, said oxidizing action being effected at a temperature in the range of 400 to 700° C.

6. A process for producing an organic compound consisting of carbon, hydrogen and sulphur in which all the carbon atoms of each molecule are in a straight chain, which comprises polymerizing ethylene in the presence of a nickel oxide polymerization catalyst to produce normal olefins of at least 16 carbon atoms per molecule, separating from effluents of said polymerization a fraction containing normal olefins of at least 16 carbon atoms per molecule, and reacting said fraction with free sulphur to produce a sulphurized hydrocarbon.

7. A process for producing an organic compound consisting of carbon, hydrogen and sulphur in which all the carbon atoms of each molecule are in a straight chain, which comprises polymerizing ethylene in the presence of a nickel oxide polymerization catalyst to produce normal olefins of at least 16 carbon atoms per molecule, separating from effluents of said polymerization a fraction containing normal olefins of at least 16 carbon atoms per molecule, and reacting said polymer fraction with a sulphurizing agent to form a sulphurized hydrocarbon.

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