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ANTIOXIDANTS

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The present invention relates to the production of sulfur-containing compositions possessing properties rendering them effective as antioxidants and stabilizers for organic materials. The invention relates more particularly to an improved process for the production of sulfur-containing additives for mineral oils and mineral oil-containing compositions.

Compositions of widely diverging characteristics have been proposed heretofore for rendering organic materials, for example mineral oils, mineral oil-containing compositions such as mineral oil-containing lubricants, lubricating oils and greases, resistant to oxidation. Thus, it is known that certain sulfur-containing compounds of specific composition render mineral oils, particularly those with the viscosity of a lubricating oil, and greases more resistant to oxidation and discoloration when they are dissolved in these oils and greases in small quantities. It has further been proposed that acid oils, if desired, after treatment with an adsorbent, such as silica gel, be added in small quantities to turbine oils to inhibit the oxidation of these oils and the corrosive action thereof on steam turbines.

Acid oils have been used as starting or intermediate materials in the production of lubricating oil additives. Methods disclosed heretofore are, however, often handicapped by the complexity or cost of the operational procedure involved, or by the use of operating conditions the severity of which adversely affects the desired properties of the resulting product.

It is an object of the present invention to provide an improved process enabling the efficient production of products eminently suitable as antioxidants and stabilizers for organic compositions such as, for example, mineral oils and mineral oil-containing lubricants and greases, from "acid oils."

A further object of the invention is the provision of an improved process enabling the production at substantially increased production rates of antioxidants of the desired characteristics from readily available acid oils at more moderate temperature conditions.

In accordance with the present invention "acid oil" is reacted with an alkali metal hydroxide and a halo-hydrocarbon having a number of halogen atoms in the range of from two to twice the number of carbon atoms in the halo-hydrocarbon at a temperature of from about 70° C. to about 140° C. The use of a temperature of from 90 to 110° C. is generally preferred. At these temperatures the reaction is generally completed in from about two to about six hours.

An advantage of the present invention resides in the fact that the conditions used result in the obtaining of antioxidant products having a considerably higher sulfur content and, consequently, increased effectiveness as antioxidants as compared with products often produced from acid oils by methods available heretofore.

By the term "acid oil" as used in the present specification and appended claims is meant the thiophenol-containing composition obtained by acidifying the aqueous

phase resulting from the contacting of a thermally and/or catalytically cracked gasoline with an alkaline solution, for example, a 10 to 20% aqueous alkaline metal hydroxide solution. During treatment of a cracked gasoline with an aqueous alkali metal hydroxide solution of 10 to 20% concentration only very small proportions of any aliphatic mercaptans present in the gasoline pass into the resulting aqueous phase, due to the very weakly acid nature of the aliphatic mercaptans. Production of the "acid oil" containing thiophenols and phenols from the aqueous phase obtained by contacting cracked gasoline with aqueous alkali metal hydroxide solution may take place, for example, in the following manner.

Any entrained gasoline is removed from the aqueous phase resulting from the treatment of cracked gasoline with the aqueous alkaline solution, by distillation, in the presence of added steam if desired. The remaining alkaline solution is then acidified with a strong acid, for example sulphuric acid, so that two phases are formed, an upper phase containing thiophenols and phenols and a lower aqueous phase. The upper phase is rid of any acid still present therein by washing. A concentrated, for example saturated, sodium chloride solution is suitable for this purpose. After the thiophenol and phenol-containing phase has been rid of acid, any resinous products are removed therefrom by distillation, the resinous products remaining behind as residue. This distillation can take place at normal or reduced pressure. The distillate is the "acid oil" reacted with the alkali metal hydroxide and the said halo-hydrocarbon, in accordance with the invention.

In interacting alkali metal hydroxide, "acid oil" and halo-hydrocarbon in accordance with the invention the alkali metal hydroxide is employed in substantially stoichiometrical equivalent amount with respect to the quantity of thiophenols present in the acid oil. The thiophenols are stronger acids than the corresponding phenols, so that when adding alkali metal hydroxide in an amount which is substantially equivalent to the stoichiometrical equivalent of thiophenols present, at least a substantial part of the thiophenols are converted to the corresponding thiophenolates, while any phenols present remain largely unconverted. By substantially equivalent stoichiometrical amount it is intended to include a range in which a slight excess of alkali metal hydroxide is used, for example, an excess of 10 to 20% over the true stoichiometrical equivalent of the thiophenols present in the acid oil.

As alkali metal hydroxide there is preferably employed an aqueous or alcoholic solution of sodium or potassium hydroxide. Examples of suitable alkali metal hydroxide solutions are of sodium or potassium hydroxide in water, methyl alcohol, or ethyl alcohol, or in mixtures of water with methyl alcohol or with ethyl alcohol, in which solution the alkali metal hydroxide has a normality of from about 1 to about 6, and preferably from about 2 to about 4.

The halo-hydrocarbons can be added to the acid oil either simultaneously with the alkali metal hydroxide, or after the acid oil has been reacted with the alkali metal hydroxide to form a reaction mixture comprising thiophenolates from the thiophenols originally present. Since the reaction of the halo-hydrocarbons with the thiophenolates proceeds considerably faster than the corresponding phenolates, the halo-hydrocarbons will react almost exclusively with the thiophenolates when the halo-hydrocarbons are employed in an amount not exceeding substantially the stoichiometrical equivalent of the thiophenolates. This will still be the case even when a relatively small quantity of phenolates has been formed during the treatment of the acid oil with the alkali metal hydroxide. Since products resulting from the interaction of halo-

hydrocarbons with thiophenolates, and not those resulting from reaction of halo-hydrocarbons with phenolates, and components of the final product which are effective as antioxidants, the halo-hydrocarbons are preferably employed in an amount which does not substantially exceed the stoichiometrical equivalent of thiophenolates present. Here stoichiometrical equivalent relates to the case in which each of the halogen atoms in the halo-hydrocarbons react with a molecule of thiophenolate.

Of the halo-hydrocarbons in which the total number of halogen atoms is at least two and not more than twice the number of carbon atoms in the molecule, those having ten or less carbon atoms, are preferred. The hydrocarbon chain of the halo-hydrocarbons may be branched or not. Preferred halo-hydrocarbons comprise those wherein the halogen atoms are distributed over the chain in such a way that terminal carbon atoms are directly attached to less than three halogen atoms. The halogen atoms comprised in the halo-hydrocarbon molecule may all be the same, for example chlorine, or may comprise different halogen atoms, so that, for example, chlorine atoms as well as bromine and/or iodine atoms may be present in a single halo-hydrocarbon molecule. Examples of suitable halo-hydrocarbons are dichloromethane, dichloroethane, 1,1,2-trichloroethane, dibromomethane, 2,5-dibromo-2,5-dimethylhexane. Mixtures of halo-hydrocarbons may be employed.

Reaction of the thiophenolates-containing composition which was obtained by reacting acid oils with alkali metal hydroxide, with the halo-hydrocarbon at moderately elevated temperatures will generally be completed within a few hours; the desired reaction product being obtained in good yields. Reaction temperatures in the range of from about 70 to about 140° C. and, more preferably from about 90 to about 110° C. are suitable, although a specific advantage of the present invention is the ability to obtain the desired antioxidants in good yields at relatively low temperatures. Higher temperatures, for example up to about 200° C. may be employed within the scope of the invention. If the reaction is executed at a temperature above the boiling temperature of alcohol or water present in the reaction mixture, superatmospheric pressures are preferably maintained in the reaction zone. Elimination of lighter components from the reaction mixture to any undesired extent during the reaction, is obviated by the use of such means as reflux condensers or coolers discharging condensate into the reaction zone.

The reaction may be carried out in an inert atmosphere, for example an oxygen-free gas, such as nitrogen.

Upon completion of the reaction the reaction mixture is processed to remove therefrom any excess alkali metal hydroxide, solvent used for the alkali metal hydroxide, and any other components which have not participated directly in the reaction, as well as alkali metal halide and water formed during the course of the reaction. Any high boiling reaction products such as resinous materials are also separated from the final reaction mixture. The reaction mixture may, for example, be worked up as follows:

If the alkali metal hydroxide was employed as an alcoholic solution, a quantity of water is first added to the cooled reaction mixture so that a separation into two phases takes place. The added quantity of water is preferably from about 30 to about 100% by weight (calculated) of the reaction mixture. If the alkali metal hydroxide has been employed in the form of an aqueous solution, the reaction mixture will have separated into two phases during the course of the reaction. In this case it is not necessary to add more water at the end of the reaction. However, if desired, water may still be added to the reaction mixture at the end of the reaction in order to assure better phase separation.

The lower aqueous phase is discarded and the upper phase is mixed with a suitable hydrocarbon diluent. A suitable diluent comprises, for example, a gasoline having a maximum boiling temperature of about 100° C. The diluent is preferably added in an amount equal to from about 25 to about 100% by weight, calculated on the acid oil employed.

After the product has been mixed with the diluent, it is washed with water to remove alkali metal hydroxide and any alkali metal halide formed during the reaction which have not been eliminated during previous steps of product recovery. A small quantity of a diluent acid, for example sulphuric acid, is then added to the mixture to neutralize any traces of alkali metal hydroxide which may still be present.

Thereupon the mixture is distilled to remove the added hydrocarbon diluent and any other low boiling components, such as any unreacted phenols originally present in the acid oil charge. The diluent can be removed by distillation under normal pressure. Since other low boiling components which are to be removed generally boil at a higher temperature than the diluent, it is preferred to carry out the distillation, at least after removal of the diluent, at a reduced pressure, for example a pressure of from about 10 to about 20 mm. Hg.

After the diluent and other lighter components have been expelled from the mixture, distillation may be continued, if desired at a still lower pressure, for example, a pressure of from about 1 to about 10 mm. Hg, in order to recover the desired final reaction product as a distillate. Residual material will then generally consist of a dark-colored resinous product which is not suitable for use in mineral oils or lubricants containing such oils.

In some cases, particularly when the process has been executed by initially reacting the acid oil with an aqueous solution of alakli hydroxide instead of an alcoholic solution, it is at times preferred to separately recover a further fraction of the distillate ("intermediate distillate fraction") which passes overhead just after the unreacted components and before the desired final products to be used as additives in mineral oils or lubricants containing such oils. The intermediate distillate fraction, which is less suitable as an additive for mineral oils or lubricants containing such oils, may, for example, amount to from about 4 to about 8% by weight calculated on the initial acid oil.

The reaction products obtained in the manner indicated often have an unpleasant odor. This odor can be removed by treating the reaction product at normal or elevated temperature with an alcoholic caustic soda solution, for example a 1-n solution of sodium hydroxide in ethyl alcohol of 96% concentration. This treatment can take place by agitating the reaction product with the alcoholic caustic soda solution. A more efficient method consists of heating the reaction product with the alcoholic caustic soda solution, for example in a quantity of 30 to 100% by weight calculated on the reaction product, for a period of about one half to two hours in a vessel provided with a reflux condenser. After the mixture has been cooled, the phase consisting of the alcoholic caustic soda solution is discarded and the remaining reaction product is washed to remove any caustic soda solution still present therein. The washing may be carried out with a mixture of water and alcohol, for example ethyl alcohol of 80% concentration. Finally, the product is dried by heating at a reduced pressure.

The products obtained in the manner described have a high sulphur content (generally 20% or more). Their use in even a slight concentration markedly increases the oxidation stability of mineral oils, lubricants containing mineral oils such as insulation oils (for example transformer oils), lubricating oils and greases. Generally, concentrations of from about 0.001 to about 1% by weight, calculated as the sulphur content of the additive, are suitable.

The amount in which the products of the process of the invention is preferably added to a specific mineral oil or mineral oil-containing composition, such as electrical oils, insulating oils, transformer oils, lubricating

oils, and the like will vary in accordance with the characteristics of the specific oil. In general it is preferred to add the compositions produced in accordance with the invention in an amount ranging from about 0.005 to about 0.1% by weight based on the sulfur content of the addition agent in the case of oils such as electrical oils, transformer oils and the like to obtain a desired antioxidant and stabilizing effect. In lubricating oils the additives are preferably used in amounts ranging from about 0.01 to about 0.2% by weight, based upon the sulphur content of the added composition.

The compositions produced in accordance with the invention may also be used in mineral oils or lubricants containing other additives. Examples of such other additives are the so-called extreme pressure dopes, viscosity index improvers, agents for improving color, pour point reducers, detergents, anti-ring-sticking dopes, etc. The products obtained by means of the process of the invention may also be used in combination with other antioxidants.

The following examples are illustrative of the invention.

Example I

One kilogram of acid oil obtained by acidifying the spent aqueous sodium hydroxide phase resulting from the treating of a Dubbs-cracked gasoline in the manner described above, and which had a mercaptan sulphur content (consisting almost entirely of aromatic mercaptans, i. e. thiophenols) of 7.87% calculated as S was used as a starting material. To this acid oil were added 1.23 liters of a 2-n ethyl alcohol solution of potassium hydroxide (this quantity being 20% more than the stoichiometrical equivalent of the mercaptan sulphur), and 110 grams of dichloro-ethane (this quantity being 90% of the amount calculated as the stoichiometrical equivalent of the mercaptan sulphur content of the acid oil).

The reaction mixture was heated for two hours in a nitrogen atmosphere in a vessel provided with a reflux condenser at a temperature of 100° C., and subsequently cooled, again in a nitrogen atmosphere.

1.2 liters of water were then added to the mass, the mixture thereupon separating into two phases. The lower phase was discarded and the upper phase was mixed with 750 cc. of gasoline with a boiling range of 60 to 80° C.

The gasoline solution was washed with water to remove any potassium hydroxide still present and the potassium chloride formed during the reaction, after which the last traces of potassium hydroxide were neutralized with dilute sulphur acid.

The mixture was then heated on a steam bath, to distill the gasoline therefrom. Distillation was continued under reduced pressure to remove phenols and unconverted thiophenols. In this way 164 grams of a distillate fraction passed overhead between 70 and 185° C. at 14 mm. Hg. Distillation was continued and a 231 gram fraction was collected which distilled over between 185 and 233° C. at 14 mm. Hg.

In order to improve the odor of the 231 gram fraction, which was a light-colored oil, 115 grams of 1-n alcoholic potassium hydroxide solution were added thereto and the mixture was refluxed for an hour.

After the mixture had been cooled, the alcoholic potassium hydroxide solution phase was discarded and the product phase was washed with an aqueous solution of ethyl alcohol of 80% concentration to remove any potassium hydroxide solution still present. The product was finally dried for half an hour at a temperature of 100° C. at reduced pressure (20 mm. Hg). The dried product constituted the desired end product, which was obtained in a yield of 70% calculated on the dichloro-ethane used. The product had an S content of 24% and a Cl content of 0.01%.

Example II

The initial material used was 1 kilogram of an acid oil obtained by acidifying the spent aqueous caustic phase produced in treating with aqueous NaOH, as described above, a catalytically cracked gasoline. The acid oil had a mercaptan sulphur content (consisting almost entirely of aromatic mercaptans) of 8.07% by weight, calculated as S. To this acid oil were added 1.51 liters of a 2.00-n aqueous potassium hydroxide solution (this quantity corresponding to an excess of 20% with respect to the mercaptan sulphur content of the acid oil), and also 125 grams of dichloroethane (i. e. the theoretical equivalent quantity calculated on the mercaptan sulphur content of the acid oil). The mixture was heated for two hours in a nitrogen atmosphere at a temperature of 105° C. in a vessel provided with a reflux condenser, after which the mixture was cooled, also in a nitrogen atmosphere. Subsequently, the lower phase which had formed during the reaction was separated off and removed from the reaction mixture. The upper phase was worked up in the manner indicated in Example I by diluting this phase with gasoline, washing it with water, neutralizing the last traces of potassium hydroxide solution with dilute sulphuric acid, and removing the gasoline by distillation on a steam bath.

The product thus obtained was then distilled at a pressure of 14 mm. Hg. A 616 gram fraction with a boiling range of 75 to 190° C., containing the unconverted components of the acid oil, distilled off first. A 57 gram fraction which distilled over at the pressure of 14 mm. Hg. between 190 and 225° C. was then collected. This 57 gram fraction was also discarded. By continuing the distillation a 254 gram fraction was obtained which distilled over at between 225 and 237° C. at 14 mm. Hg.

To improve the odor of the 254 gram fraction it was heated with alcoholic potassium hydroxide solution in a vessel provided with a reflux condenser in the manner indicated in Example I. After the product had been freed of alcoholic potassium hydroxide solution in the manner indicated in Example I, the desired end product was obtained in a yield of 60%, calculated on the dichloroethane used. This end product had an S content of 23.6% and a Cl content of less than 0.05%.

Example III

The initial material used was 500 grams of an acid oil, obtained during the refining with aqueous NaOH of a Dubbs-cracked gasoline, and which had a mercaptan sulphur content (consisting almost entirely of aromatic mercaptans) of 7.59%. To this were added 745 cc. of a 1.91-n solution of KOH in ethyl alcohol and 50 grams of dichloro-methane. The reacting of the mixture and the working up of the reaction product were carried out in the manner described in Example I.

During the distillation carried out after the reaction product had been worked up, the desired fraction distilled over between 230 and 240° C. at a pressure of 16 mm. Hg. The yield of this fraction was 113 grams.

Finally, this fraction was treated with alcoholic potassium hydroxide solution to improve the odor in the manner indicated in Example I. The end product was obtained in a yield of 64% by weight, calculated on the dichloro-methane used. The S content of the product was 24.2% and the Cl content was less than 0.01%.

Example IV

The initial material used was 500 grams of an acid oil, obtained during the refining with aqueous sodium hydroxide of Dubbs-cracked gasoline, and which had a mercaptan sulphur content (consisting almost entirely of aromatic mercaptans) of 7.59%. To the acid oil there were added 53 grams of trichloro-ethane and 377 cc. of a 3.77-n aqueous potassium hydroxide solution. After the mixture had been kept for six hours in a nitrogen atmosphere at distillation temperature (1705° C.) in a vessel provided with a reflux condenser, the reaction product thus ob-

tained was worked up in a manner similar to that described in the previous examples.

The product was worked up substantially as described in Example I. The final product distilled over between 160 and 180° C. in a quantity of 20 grams at a pressure of 2 mm. Hg. The S content of this product was 24.8% and the Cl content less than 0.05%.

Example V

Each of the reaction products obtained as described in the foregoing Examples I–IV was added in an amount of 0.02% by weight, calculated as S, to different samples of the same lubricating oil. This oil was a Venezuelan lubricating oil distillate, which had been intensively extracted with SO_2 and subsequently treated with 10% of oleum. The improvement in the oxidation stability of the lubricating oil as a result of the addition of the products of the preceding examples was determined according to the B(ritish) S(tandards) I(nstitution) test 148/51, the result being given in the following table.

Additive (concentration 0.02% calculated as S)	Results of B. S. I. test	
	Percent by weight of sludge formed	Acid No.
None	0.86	2.1
Product of Example I	0.41	0.4
Product of Example II	0.39	0.4
Product of Example III	0.41	0.4
Product of Example IV	0.94	1.2

Example VI

Tests analogous to those described in Example V were carried out with a Venezuelan lubricating oil distillate which had been extracted to a moderate degree with SO_2 and thereafter treated with 3% by weight of bleaching earth ("Filtrol") at 120° C. In different samples of this lubricating oil one of the reaction products of Examples I, III and IV was dissolved in an amount of 0.05% calculated as S. The results obtained were as follows:

Additive (concentration 0.02% calculated as S)	Results of B. S. I. test	
	Percent by weight of sludge formed	Acid No.
None	1.03	1.7
Product of Example I	0.75	1.2
Product of Example III	0.74	1.3
Product of Example IV	0.88	1.4

The invention claimed is:

1. The process for the production of sulfur-containing, aromatic, mineral oil additive composition from aromatic mercaptan-containing acid oils obtained by acidification of the aqueous phase formed in the treatment of aromatic mercaptan-containing cracked gasolines with aqueous alkali metal hydroxide, which comprises reacting said acid oil with alkali metal hydroxide and a halogen substituted saturated aliphatic hydrocarbon having from one to ten carbon atoms to the molecule containing a number of halogen atoms ranging from two to twice the number of carbon atoms in the halo-hydrocarbon molecule at a temperature of from about 70 to about 200° C. for a period of about 2 to about 6 hours, said alkali metal hydroxide and said halo-hydrocarbon each being present in an amount equal to the stoichiometrical equivalent of the aromatic mercaptan content of said acid oil, and distilling uncoverted acid oil components and resinous by-products from the resulting reaction products.

2. Process in accordance with claim 1 wherein said halo-hydrocarbon is a chloro-hydrocarbon.

3. Process in accordance with claim 1 wherein said halo-hydrocarbon is an alkylchloride.

4. Process in accordance with claim 1 wherein said halo-hydrocarbon is dichloroethane.

5. The process for the production of sulfur-containing, aromatic, mineral oil additive compositions from aromatic mercaptan-containing acid oils obtained by acidification of the aqueous phase formed in the treatment of aromatic mercaptan-containing cracked gasolines with aqueous alkali metal hydroxide, which comprises reacting said acid oil with potassium hydroxide and an alkyl chloride having no more than ten carbon atoms to the molecule and containing a number of chlorine atoms ranging from two to twice the number of carbon atoms in said alkyl chloride molecule at a temperature of from about 70 to about 140° C. for a period of from about 2 to about 6 hours, said potassium hydroxide and said alkyl chloride each being present in an amount equal to the stoichiometrical equivalent of the aromatic mercaptan content of the acid oil, and distilling unconverted acid oil components and resinous by-products from the resulting reaction mixture.

6. The process in accordance with claim 5 wherein said reaction is executed at a temperature in the range of from about 70° C. to about 140° C.

7. The process in accordance with claim 6 wherein said alkyl chloride is dichloroethane.

8. The process in accordance with claim 7 wherein said potassium hydroxide is employed in the form of a alcoholic solution having a normality of from about one to about six.

9. The process for the production of sulfur-containing, aromatic, mineral oil additives from aromatic mercaptan-containing acid oils obtained by acidification of the aqueous phase formed in the treatment of aromatic mercaptan-containing cracked gasolines with an aqueous alkaline solution, which comprises reacting said acid oil with potassium hydroxide and an alkyl chloride having no more than ten carbon atoms to the molecule and containing a number of chlorine atoms in the range of from two to twice the number of carbon atoms in the alkyl chloride molecule at a temperature of from about 70 to about 140° C. for a period of time of from about 2 to about 6 hours, said potassium hydroxide and said alkyl chloride each being present in an amount equal to the stoichiometrical equivalent of the aromatic mercaptan content of the acid oil, distilling unconverted acid oil components and resinous by-products from the resulting reaction mixture, and contacting the remaining reaction mixture with an alcoholic alkaline solution.

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