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PROCESSES FOR PURIFYING SULFURIZED HYDROCARBON PRODUCTS

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The present invention relates to sulfurized hydrocarbon products which have utility as addition agents for lubricants and the like and relates more specifically to a method for purifying such products.

It is known that excellent addition agents for lubricating oils may be prepared by sulfurizing olefin hydrocarbons, especially the polymers of low molecular weight olefins such as the polymers of propylene, butylenes, amylenes and the like. Although these materials may be sulfurized by heating with free sulfur, a more satisfactory product from the standpoint of oil solubility, lack of copper staining tendency and odor can be obtained by sulfurizing with a sulfur halide, such as sulfur monochloride or sulfur dichloride. It is difficult to free the resulting product from a considerable proportion of the halogen. Amounts of halogen as high as 10% or greater remain in the sulfurized product even after heating for long periods of time. Such amounts of halogen are quite objectionable, particularly where corrosion is to be avoided.

One procedure that has been used successfully for dehalogenating such products has been that of heating the material with an aromatic compound such as a phenol. This step drives off subtsantially all of the chemically combined halogen and forms a product that is not excessively corrosive to metals. The phenols and other related aromatic compounds, however, form degradation products which remain as dark colored bodies in the final product. It is difficult to remove the degradation products, and lubricants containing the additive are impaired in color and copper staining tendency. This adversely affects the marketability of such lubricants.

It is also known to treat the sulpho-halogenated product described above with catalytic amounts of secondary or tertiary saturated monohydric aliphatic alcohols in order to form an improved product. Although this mode of treatment forms a product of relatively good color characteristics, the alcohols are generally not sufficiently effective catalysts to reduce the halogen to commercially acceptable values. In general, it is desired to produce compounds containing less than about 2 to 3% halogen, preferably below 1% halogen. It is usually not possible to accomplish this with the monohydric alcohols even when using excessive amounts of alcoholic treating agents or severe treating conditions that generally cannot be tolerated in commercial operations.

In accordance with the present invention, an aliphatic or cycloaliphatic hydrocarbon that has been sulfurized by means of a sulfur halide can be dehalogenated with little difficulty by merely heating such product containing hydrogen halide impurities with a non-aromatic organic compound containing at least two hydroxyl groups. Such polyhydroxy compounds are not only superior to phenols and monohydroxy aliphatic alcohols as dehalogenation agents under comparable treating conditions, but they also form products having excellent color characteristics and little tendency to stain copper and are superior in these respects to the prior art products.

Advantageous results may be obtained by employing quantities of the polyhydroxy compounds ranging from about 1 to 25% by weight, preferably 3 to 15% by weight, based on the sulfurized hydrocarbon product. The treating temperature range that may be employed is from about 100° to about 350° F., more preferably from about 175° to 300° F. It will generally be found convenient to conduct the treating operation at a reduced pressure for times in the range of about 0.5 to 10 hours in order to insure substantially complete removal of halogen. After the heating step, the product may be steamed, blown with an inert gas or otherwise treated to remove any traces of unreacted hydrocarbon, hydrogen halide or other contaminating materials.

It is not desired to be bound by theoretical considerations, but apparently the action of the polyhydroxy compound in effecting dehydro-halogenation is mainly catalytic. A small proportion of the polyhydroxy material, however, may enter into chemical combination with the sulfurized hydrocarbon.

The hydrocarbon materials, which may be sulfurized by sulfur halides and then reduced in halogen content by the method of the present invention, include any aliphatic or alicyclic hydrocarbons containing an unsaturated carbon-to-carbon linkage. This group of materials includes the olefins, e. g., propylene, butylenes, diisobutylenes, triisobutylenes, the codimer of isobutylene and n-butylene, carcked gasoline fractions, cracked paraffin wax, viscous olefin polymers such as medium or high molecular weight polybutene, cyclopentene, cyclohexene, butadiene, pentadiene, isoprene and the like. Likewise the process may be applied to compounds having acetylenic linkages, C≡C. Olefins of less than 4 carbon atoms are not generally employed in preparing sulfurized lubricating oil additives, although products prepared from such olefins may be purified by the method of the present invention. Derivatives of the above described compounds containing various substituent groups and atoms may be used to advantage since the substituent groups normally do not interfere with the sulfurization reaction or the purifying process herein described. Such substituted derivatives may include olefins having attached aromatic nuclei, halogen atoms, nitro groups, etc.

For the preparation of the sulfurized hydrocarbons and the like, the most suitable sulfur halides are sulfur dichloride and monochloride, especially the latter. The olefinic material and sulfur halides are generally reacted in ratios of olefinic material to sulfur halide within the range from about 3:1 to 1:1 molal ratio. Higher ratios of olefinic material are sometimes used when a portion of the same is to serve as a solvent to be removed later as unreacted material. The temperatures which have been found most satisfactory for this reaction are from about 70° to 125° F., but the method may be carried out at considerably higher or lower temperatures if desired. Catalysts are not required.

The polyhydroxy organic compounds which may be employed as dehalogenation catalysts in the present invention are preferably polyhydroxy aliphatic and alicyclic alcohols, although compounds containing ether linkages between carbon atoms, such as polyhydroxy ether alcohols or those containing other substitutent groups may also be used. Such compounds may contain 2, 3, 4 or even more hydroxyl groups in the molecule. They may be straight chain or branched in character and may have low, medium or high molecular weights. Suitable compounds include ethylene glycol, propylene glycol, 1,2-butanediol, glycerol; erythritol; erythrol; pentaerythritol; diethylene glycol; triethylene glycol; dipropylene glycol; octylene glycol; 1,10-decanediol; 1,2-cyclopentanediol; and the like. The higher molecular weight polyhydroxy compounds include such materials as polyethylene glycols hav-

ing molecular weights as high as 200, 500, 1,000, 6,000, and higher.

The most effective compounds of this class are generally those having in the range of 3 to 20 carbon atoms, preferably in the range of 5 to 12 carbon atoms. The above is only a partial list of the types of materials that may be used in the practice of the present invention, and it will be obvious to the skilled workman that other compounds of this general class may be selected for practicing the invention.

The following examples illustrate the application of the present invention in purifying a sulfurized diisobutylene. These examples, however, are not to be considered as limiting the scope of the invention in any manner.

Example 1.—Comparison of various hydroxy compounds as dehalogenation agents

Product A.—This product was prepared in a 3-liter 4-necked flask equipped with a mechanical agitator, dropping funnel, thermometer and gas outlet. 975 g. of diisobutylene were placed in the flask and 391 g. of sulfur monochloride was added slowly over a period of one hour at a temperature of 72° to 115° F. After agitating for one hour at approximately 100° F., 44 g. of octylene glycol (5.3% by weight, based on the sulphochlorinated material) was added and heat was applied to the reaction mixture. Distillation equipment was attached to the flask in order to take over any evolved gas, excess diisobutylene, and light ends. The material was heated to a temperature of 230° F., vacuum was applied slowly to the system and the reaction mixture was held at 400 mm. Hg absolute for 6 hours at this temperature. At the end of this time, the reaction mixture was steamed to remove any traces of diisobutylene, hydrogen chloride and light ends. The product was then dried.

Product B.—This product was prepared by the procedure used in preparing Product A except that 44 g. of phenol were used in place of octylene glycol as the dehalogenation catalyst.

Product C.—This product was prepared by the procedure used in preparing Product A except that 44 g. of 2-ethyl-hexyl alcohol were used in place of octylene glycol as the dehalogenation agent.

Each of the above products were analyzed for sulfur and chlorine contents, and Tag-Robinson colors were determined on mixtures containing 25% of the product in a light hydrocarbon, water white solvent. Copper strip staining ratings were also determined. Pertinent yield, analytical and other inspection data are shown in Table I below:

TABLE I

Product	Catalyst	Product Yield, Weight Percent	Inspections on Finished Product				
			Sulfur, Weight Percent	Chlorine, Weight Percent	Tag-Robinson Color (25% in Solvent)	Saybolt Vis. @ 100° F.	Copper Strip, 3 Hrs. @ 212° F. 0.5% in Oil [1]
A	Octylene Glycol	89	21.6	0.3	11½	54.9	Light Peacock.
B	Phenol	87	22.6	0.9	⅞	61.7	Black Deposit.
C	2-Ethyl Hexanol	85	24	4.9	10	62.9	Light Peacock.

[1] SAE-20 grade mineral lubricant.

The octylene glycol was superior to either phenol or 2-ethyl hexanol as a dehalogenation catalyst both as regards chlorine content and yield of product. The glycol also produced a material having markedly superior color characteristics to that produced when using phenol as catalyst and somewhat better than that when using the monohydroxyl alcohol. Also the glycol produced a material markedly superior in copper staining tendencies to the material produced by phenol catalyst. It is interesting to note that the chlorine content of the alcohol-treated product was approximately 16 times greater than that obtained when using the glycol.

Example 2

A series of runs were carried out under conditions similar to those used in preparing Product A. The amount of the octylene glycol catalyst was varied in the range of 2.5 to 10% by weight, based on the sulphochlorinated material. Maximum reaction temperatures in the presence of the glycol were also varied. The results of these runs are shown in Table II below:

TABLE II

Dehalogenation Temperature, °F.	Octylene Glycol Used, Weight Percent	Product Analysis, Weight Percent	
		Chlorine	Sulfur
300	10	0.6	22.6
300	10	0.6	21.8
300	5	2.0	22.3
250	5	0.9	24.0
250	5	1.1	24.0
230	10	1.5	22.4
230	5	0.3	21.6
230	2½	3.6	22.0

Example 3

A series of runs were carried out using procedures similar to those described in the preparation of Products A, B and C with the exception that various other polyhydroxy compounds, alcohols and aromatic compounds were employed as catalysts. In most cases, 10% by weight of catalyst, based on the product treated, was used. The results are tabulated in Table III as follows:

TABLE III

Catalyst Employed	Inspections on Final Product		
	Chlorine, Weight Percent	Sulfur, Weight Percent	Tag-Robinson Color (25% in Solvent)
Polyhydroxy Aliphatic Compounds:			
Ethylene glycol	3.3	23.1	10¼
Propylene glycol	1.3	24.6	9+
Diethylene glycol	1.7	24.7	10
Triethylene glycol	1.6	24.4	10
Dipropylene glycol	1.5	23.7	9+
Polyethylene glycol (6,000 avg. mol. wt.)	2.4	23.2	12¼
Phenols:			
Tri-amyl phenol	0.7	22.0	¾
Hydroquinone	2.1	(1)	[1] (dark)
Alcohols:			
Isopropyl [2]	3.2	17.0	(1)
C_{16}–C_{18} Alcohols [3]	1.7	21.5	3¾

[1] Not determined.
[2] Used 40% by weight of alcohol, based on treated product.
[3] "Lorol B" alcohols having average molecular weight of about 207.

Each of the aliphatic polyhydroxy catalysts produced final products having excellent color characteristics and realtively low chlorine contents. Ethylene glycol and polyethylene glycol having a molecular weight of about 6,000 were not quite so effective as the glycols of intermediate molecular weight. It is noted that the polyhydroxy aromatic compound, hydroquinone, was inferior to the polyhydroxy aliphatic compounds with respect to product color. Isopropyl alcohol was inferior to propylene glycol with respect to its dehalogenation effectiveness. The higher alcohols as represented by the C_{12}–C_{18} alcohols degraded the color of the final product.

The present invention is not to be considered as limited by any of the specific embodiments or examples herein disclosed, but is to be limited solely by the terms of the appended claims.

What is claimed is:

1. A method of dechlorinating a sulfurized olefin which has been obtained by reacting a member selected from the group consisting of olefins and polymers thereof with a sulfur chloride, which comprises heating said sulfurized olefin in the presence of a polyhydroxy aliphatic organic compound containing from 3 to 20 carbon atoms at a temperature in the range of about 100° to about 350° F.

2. A method as in claim 1 wherein said polyhydroxy compound contains 2 hydroxyl groups.

3. A method as in claim 2 wherein said polyhydroxy compound is propylene glycol.

4. A method as in claim 2 wherein said polyhydroxy compound is diethylene glycol.

5. A method as in claim 2 wherein said polyhydroxy compound is triethylene glycol.

6. A method as in claim 2 wherein said polyhydroxy compound is dipropylene glycol.

7. A method as in claim 2 wherein said polyhydroxy compound is octylene glycol.

8. A method of dechlorinating sulfurized diisobutylene which has been formed by reacting diisobutylene with a sulfur chloride which comprises reacting said sulfurized diisobutylene in the presence of about 1 to 25% by weight of a glycol having in the range of 5 to 12 carbon atoms at a temperature in the range of about 100 to 350° F.

9. A method of dechlorinating sulfurized diisobutylene which has been obtained by reacting diisobutylene with sulfur monochloride which comprises heating said sulfurized diisobutylene with octylene glycol at a temperature in the range of about 175° to 300° F., for a period in the range of about 0.5 to 10 hours, said glycol being used in an amount in the range of 3 to 15% by weight, based on said sulfurized diisobutylene.

10. As a new composition of matter, the product produced by the process of claim 1.

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