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PROCESS OF SULPHURIZATION

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This invention relates to the sulphurization of organic substances, more particularly to the sulphurization of oils and fats.

As is well known, sulphurized fatty and mineral oils have been extensively used in the manufacture of cutting oils and lubricants. Sulphurized fatty oils have heretofore been made by heating sulphur with a fatty oil whereby a certain amount of sulphur was taken up by the fatty substance. This method has proved to be extremely disadvantageous because invariably the product obtained has a very dark color and a highly unpleasant odor. It has been practically impossible to prepare sulphurized mineral oils directly because mineral oils upon heating with sulphur do not take up sufficient quantities thereof to effect the production of suitable sulphurized oils. Therefore, sulfurized mineral oils have heretofore been prepared by first manufacturing a sulphurized fatty base as above described, and then adding the base to the mineral oil. Such sulphurized mineral oils possess the same disadvantages that the sulphurized fatty substances possess; namely, they are extremely malodorous and possess very dark colors. Many attempts have been made to improve the colors and odors of sulphurized oils and fats, but as yet no commercially satisfactory method has been worked out.

It is an object of this invention to provide sulphurized organic substances which do not have objectionable colors and odors.

It is a more specific object of this invention to prepare sulphurized oils and fats free of obnoxious odors and having relatively light colors.

We have found that sulphurized organic substances free of obnoxious odors and having relatively light colors may be manufactured by reacting a normally liquid sulphur halide with ammonia in the presence of an organic substance having a melting point below the boiling point of the sulphur halide employed. The reaction of ammonia with the sulphur halide produces sulphur, and the sulphur is immediately taken up by the organic substance so as to form sulphurized products having the desirable characteristics above mentioned. The ammonium halide formed by the reaction between the ammonia and sulphur halide may be removed from the sulphurized substance in any suitable manner. Our invention is particularly applicable to the preparation of sulphurized oils and fats for use in the manufacture of cutting oils and lubricants; these sulphurized oils and fats are completely free of obnoxious odors and have rela-

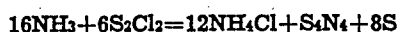
tively light colors, and hence are far superior to sulphurized oils and fats now on the market. Furthermore, the process of our invention may be employed for sulphurizing mineral oils, thus obviating the necessity of preparing sulphurized fatty bases in order to obtain sulphurized mineral oils. Cutting oils and lubricants prepared from the sulphurized products of our invention are at least as effective as similar products prepared from present commercially available sulphurized substances and are superior to such products in that they do not possess objectionable colors and odors. Our invention also permits the sulphurization of a large number of organic substances other than oils and fats so that new sulphurized products possessing valuable properties may be obtained thereby.

Any organic substance having a melting point below the boiling point of the particular sulphur halide employed may be sulphurized in accordance with our invention. Our invention is particularly adapted to the production of sulphurized oils, fats and waxes; thus oils, fats and waxes of animal, vegetable or marine origin such as teaseed oil, olive oil, rice bran oil, castor oil, lard oil, cod oil, sperm oil, pine oil, wool grease, etc., may all be sulphurized. One of the important features of our invention is that it permits direct sulphurization of mineral oils; for example, petroleum products such as paraffin oil, heavy lubricating oils, naphthenic acids and oxidized petroleum fractions may be sulphurized thereby. Other organic substances which might advantageously be sulphurized in accordance with our invention by employing proper conditions of operation include fatty acids, fatty alcohols, blown fatty alcohols, blown oils, esters, mono and diglycerides, fatty amides, ketones, ethers and nitriles.

The process of our invention may be carried out by contacting ammonia with a normally liquid sulphur halide in the presence of the organic substance to be sulphurized. The term "normally liquid sulphur halide" is employed throughout the specification and claims to include sulphur halides which are liquids at room temperature and atmospheric pressure; thus, for example, the process of our invention may be practiced by employing sulphur monochloride, sulphur dichloride, sulphur monobromide, thionyl chloride, sulphuryl chloride, or other sulphur halides liquid at room temperature and pressure. The ammonia which reacts with the sulphur halide may be introduced into the reaction mixture in the form of ammonia gas; however, we prefer to carry

out the reaction by mixing relatively strong solutions of ammonium hydroxide with the sulphur halide.

When carrying out the sulphurization process of our invention as applied to the production of sulphurized oils or fats, suitable amounts of ammonia and a normally liquid sulphur halide may be mixed in the presence of the oil or fat to be sulphurized. The oil or fat must have a melting point below the boiling point of the particular sulphur halide employed. If the substance to be sulphurized is an oil, the ammonia and sulphur halide may be introduced directly into the oil; if, however, the organic substance is a solid fat, the fat may be melted or may be dissolved in a suitable solvent and the reaction ingredients then added. The relative amounts of the reaction ingredients incorporated in the organic substance to be sulphurized may vary to some extent, but we prefer to employ a slight excess of ammonia over that necessary to react with the sulphur halide; if ammonium hydroxide is employed, as is preferred, the amount should be sufficient so that the required amount of ammonia is present in the reaction mixture. The total quantity of reacting ingredients introduced into the organic substance may vary widely, depending upon the amount of sulphur capable of being taken up by the organic substance and upon the amount it is desired to incorporate therein; the amount of sulphur capable of being taken up may vary widely and usually has to be determined empirically for each organic substance to be sulphurized. Once this amount is determined, it is a relatively simple matter to calculate the quantity of reacting ingredients to be mixed with the organic substance in accordance with stoichiometric principles. For example, if sulphur monochloride is the sulphur halide employed, the amount of sulphur produced may be calculated from the following equation denoting the probable course of the reaction:



The organic substance being sulphurized first becomes dark red; as the reaction proceeds, however, the color becomes lighter. A considerable amount of heat is evolved during the course of the reaction between the ammonia and sulphur halide; this heat ordinarily causes no difficulty. The reaction proceeds readily without heating the mass externally; however, if desired, elevated temperatures below the boiling point of the sulphur halide may be employed. The reaction is usually carried out under atmospheric pressure, but pressures above or below atmospheric may be used if desired; however, the pressure should not be so low as to cause the sulphur halide to boil. The time of the reaction may vary widely, but approximately 30 minutes is ordinarily sufficient. When the reaction is complete, solid materials contained in the mass may be removed by filtration or in any other suitable manner. If ammonium hydroxide is employed, the water may be removed by evaporation and the solids then separated from the sulphurized mass, or the sulphurized mass may be permitted to stand and the aqueous layer containing ammonium chloride withdrawn.

The sulphurized oils and fats of our invention all possess relatively light colors and are free of any obnoxious odors; thus they are far superior to sulphurized oils and fats now on the market and will find extensive use in the manufacture of cutting oils and lubricants. Sulphurized bases

may also be prepared in accordance with our invention. Products such as sulphurized pine oil may find employment in the therapeutic field; the sulphurized products of our invention may also be employed as insecticides, leather oils, flotation agents and for other uses known to the art.

While the above detailed description has been limited to the sulphurization of oils and fats, it is to be understood that our invention is applicable to the sulphurization of any organic substance having a melting point below the boiling point of the sulphur halide employed. It is to be further understood that all the sulphurized products of our invention have extremely light colors and are free of obnoxious odors, and hence will be adapted for a wide variety of uses.

The following examples are illustrative of our invention; amounts are given in parts by weight.

Example I

89 parts of paraffin oil having a specific gravity of 0.885 and 3.8 parts of sulphur monochloride were mixed. 7.2 parts of a 28% ammonia solution were then rapidly added to the mixture and the mass was strongly agitated for about 30 minutes. The temperature was then raised to 115° C. and water evaporated from the mass at this temperature. When the water had been removed, the mass was permitted to cool and was then filtered. The resulting sulphurized product had a light-yellow color, was odorless and formed an excellent cutting oil.

Example II

100 parts of sperm oil were mixed with 10 parts of sulphur monochloride and gaseous ammonia was bubbled through the mixture until the odor of the ammonia could be definitely detected. The mixture was then agitated at about 50° C. for 30 minutes, at the end of which time the solid materials were removed by filtration. The resulting sulphurized product was light-colored and odorless. Sulphurized sperm oil prepared by heating sperm oil with sulphur was black and possessed a very obnoxious odor.

Example III

96 parts of pine oil were mixed with 8.4 parts of sulphur monochloride. 16 parts of a 28% ammonia solution were then rapidly added to the mixture, the mass heated to about 105° C. and agitated at this temperature for one-half hour. At the end of this time the mixture was permitted to cool and was filtered. The resulting sulphurized product had a light amber color and a pleasant odor.

Example IV

90 parts of glyceryl mono oleate were mixed with 6.3 parts of thionyl chloride. 12 parts of a 28% ammonia solution were then added to the mixture and this mass was agitated at a temperature of about 40° C. for one hour. At the end of this time the mass was permitted to cool, the aqueous layer which separated was withdrawn and the oil then filtered. The resulting sulphurized product had a very light color and was free of obnoxious odors.

Example V

98 parts of distilled naphthenic acids having a boiling range from 220° C. to 250° C. were mixed with 21 parts of thionyl chloride. 40 parts of a 28% ammonia solution were then added to the

mixture, the mass warmed to about 40° C. and agitated at this temperature for one hour. At the end of this time the mass was permitted to cool, the aqueous layer which separated was withdrawn and the oil then filtered. The resulting sulphurized product had a very light color and was substantially odorless.

Example VI

100 parts of an amide prepared by condensing sperm oil with amyl amine were melted and the melt was mixed with 8 parts of a 28% ammonia solution. 4.2 parts of sulphur monochloride were then added to the mixture with vigorous stirring; the temperature of this mass was raised to about 120° C. and agitation was continued at this temperature for one hour. At the end of this time the mass was permitted to cool slightly and was then filtered. Upon cooling the filtrate solidified to form a light-brown, soft, sulphurized solid having a pleasant odor. This product could readily be dissolved in mineral oils to yield an excellent cutting oil.

Example VII

100 parts of oleone were mixed with 6.3 parts of sulphuryl chloride. 12 parts of a 28% ammonia solution were then added to the mixture and the mass agitated at 110° C. for one-half hour. At the end of this time the mass was permitted to cool and was then filtered. The resulting sulphurized product was light-colored and had a very pleasant odor.

Example VIII

40 parts of the methyl ester of tall oil fatty acids were mixed with 15 parts of a 28% ammonia solution. 12.6 parts of sulphur monochloride were then added to the mixture and the mass was agitated for 10 minutes at 80° C. At the end of this time the mass was permitted to cool and then filtered. The resulting sulphurized product had a light color and a very pleasant odor.

It will be evident from the above description that the process of our invention permits the production of sulphurized organic substances, the color and odor of which make them far superior to sulphurized products now on the market. Moreover, our invention permits the direct sulphurization of any organic substance, and hence constitutes a marked improvement over processes for manufacturing sulphurized products heretofore employed. Our invention will, therefore, be of great interest to those engaged in the manufacture of sulphurized products.

Since certain changes in carrying out the above process and certain modifications in the compositions which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A process for sulphurizing organic substances, which comprises reacting a normally liquid sulphur halide with ammonia in the presence of an organic substance having a melting point below the boiling point of the sulphur halide employed.

2. A process for sulphurizing oils and fats, which comprises reacting a normally liquid sulphur halide with ammonia in the presence of a substance selected from the group consisting of

oils and fats having melting points below the boiling point of the sulphur halide employed.

3. A process for sulphurizing mineral oils, which comprises reacting a normally liquid sulphur halide with ammonia in the presence of a mineral oil.

4. A process for sulphurizing organic substances, which comprises reacting sulphur monochloride with ammonia in the presence of an organic substance having a melting point below the boiling point of sulphur monochloride.

5. A process for sulphurizing organic substances, which comprises reacting thionyl chloride with ammonia in the presence of an organic substance having a melting point below the boiling point of thionyl chloride.

6. A process for sulphurizing organic substances, which comprises reacting sulphuryl chloride with ammonia in the presence of an organic substance having a melting point below the boiling point of sulphuryl chloride.

7. A process for sulphurizing oils and fats, which comprises reacting sulfur monochloride with ammonia in the presence of a substance selected from the group consisting of oils and fats having melting points below the boiling point of sulphur monochloride, and recovering the sulphurized product.

8. A process for sulphurizing oils and fats, which comprises reacting thionyl chloride with ammonia in the presence of a substance selected from the group consisting of oils and fats having melting points below the boiling point of thionyl chloride, and recovering the sulphurized product.

9. A process for sulphurizing oils and fats, which comprises reacting sulphuryl chloride with ammonia in the presence of a substance selected from the group consisting of oils and fats having melting points below the boiling point of sulphuryl chloride, and recovering the sulphurized product.

10. A process for sulphurizing mineral oils, which comprises reacting sulphur monochloride with ammonia in the presence of a mineral oil and recovering the sulphurized product.

11. A process for sulphurizing mineral oils, which comprises reacting thionyl chloride with ammonia in the presence of a mineral oil and recovering the sulphurized product.

12. A process for sulphurizing mineral oils, which comprises reacting sulphuryl chloride with ammonia in the presence of a mineral oil and recovering the sulphurized product.

13. A process for sulphurizing organic substances, which comprises forming a mixture containing a normally liquid sulphur halide, ammonium hydroxide and an organic substance having a melting point below the boiling point of the sulphur halide employed, permitting the sulphur halide to react with the ammonium hydroxide and separating water and residual solid materials formed by the reaction from the sulphurized product.

14. A process for sulphurizing paraffin oil, which comprises forming a mixture containing paraffin oil, sulphur monochloride and ammonium hydroxide, permitting the sulphur monochloride to react with the ammonium hydroxide and separating water and residual solid materials formed by the reaction from the sulphurized paraffin oil.

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