This invention relates to a process for the manufacture of valuable alkyl disulfides of high molecular weight. More specifically the present invention relates to the manufacture of high molecular-weight alkyl disulfides from high boiling olefins through the intermediate formation of mercaptans followed by selective oxidation to the corresponding disulfide. Even more specifically this invention relates to the production of valuable lubricating oil additives, comprising alkyl disulfides of high molecular weight, by an integrated process of manufacture involving the interaction of selected olefins with hydrogen sulfide to form mercaptans which are subsequently converted to disulfides by means of a novel oxidation system.

An object of this invention is to provide an integrated process for the conversion of selected olefinic hydrocarbons to high molecular-weight alkyl disulfides by means of the following sequence of operations: (1) catalytic addition of H₂S to the olefins to yield mercaptans; (2) selective oxidation of the mercaptans to the alkyl disulfides.

Another object of the present invention is to provide for the catalytic conversion of high-boiling olefinic feed stocks to the corresponding mercaptan derivative which may be oxidized to disulfides with a minimum of purification.

A further object of this invention is to provide a novel oxidation procedure operating in conjunction with a mercaptan synthesis step to produce high molecular-weight disulfides.

A still further object of this invention is to provide a process of manufacture of high molecular-weight alkyl disulfides having desirable additive properties with respect to lubricating oils.

We have now discovered that alkyl disulfides of high molecular weight can be advantageously manufactured in a continuous process utilizing selected olefins and H₂S as the starting raw materials and combining these materials under the influence of catalysts to produce a mercaptan-containing stream which may be directly subjected to oxidation. We have also found that the recovery of unreacted olefinic hydrocarbons and/or diluents is greatly facilitated subsequent to conversion of the mercaptans to disulfides.

We have further found that the diluent effect of the non-mercaptan components in the feed feed to the oxidation reaction is beneficial as manifested in decreased foaming and in reduction of the viscosity of the effluent.

A feature of the present invention is the oxidation system employed in the conversion of high molecular-weight tertiary mercaptans to disulfides. We are aware of the extensive art dealing with the oxidation of very dilute solutions of mercaptans to disulfides as applied to the sweetening of gasoline, however virtually no information is available with respect to the relatively concentrated mercaptans in the molecular weight range of 174 to about 256 or higher. We have found that mercaptan mixtures, comprised almost exclusively of tertiary types and having average molecular weights of about 300 to 250, are very resistant to the milder oxidizing agents which normally would be expected to effect the conversion to the disulfide state. Thus, whereas it is known that the lighter mercaptans, such as those found in natural gas and gasoline, undergo an appreciable degree of oxidation to disulfides when contacted with air; the high molecular-weight tertiar mercaptans of this invention undergo substantially no oxidation when agitated with pure oxygen for several weeks. We have also observed that tertiary mercaptans having an average molecular weight of 210 remain unchanged when treated with a large excess of 30 per cent hydrogen peroxide. This behavior is in decided contrast to the known action of hydrogen peroxide in converting t-amy mercaptan to the corresponding sulfonic acid. It is apparent, therefore, that the conventional concepts pertaining to the oxidation susceptibility of mercaptans do not apply to the high molecular-weight mercaptans of this invention.

We have found that application of cupric chloride sweetening reagent to the mercaptans of this process results in a product containing excessive quantities of cuprous mercaptide indicating failure of the normal sweetening reactions. Although some disulfide could be prepared by such a reaction, the rapid failure of the oxidizing solution and the difficulties encountered in purifying the product render the procedure economically unattractive and infeasible.

We have found that whereas the high molecular-weight mercaptans herebefore described are not affected by hydrogen peroxide, the corresponding cuprous salts are readily oxidized to disulfides and cupric chloride according to the following equation:

\[ 2R\text{--Cu} + 2\text{H}_2\text{O}_2 + 4\text{HCl} \rightarrow R\text{--S--S} + 2\text{CuCl} + 4\text{H}_2\text{O} \]

We have further found that the proper combination of the copper chloride and hydrogen peroxide systems when applied simultaneously result in a smooth and substantially complete conversion of high-boiling tertiary mercaptans...
to disulfides. Thus, the two oxidizing agents, neither of which is adequate alone, mutually complement each other to produce a result which represents a distinct advance in the art of oxidation of high molecular-weight mercaptans.

A specific preferred embodiment of the present invention is illustrated in the accompanying drawing. The olefin feed may consist of a fraction of heavy polymer having from 12 to 14 or more carbon atoms per molecule which in some instances may be admixed with an inert hydrocarbon liquid. This olefin feed is withdrawn from storage tank 1 through line 2 and is blended with hydrogen sulfide from tank 3 and line 4 prior to entering reactor 5. The reactor charge composition is so adjusted that a molal excess of hydrogen sulfide prevails. Reactor 5 may comprise a catalyst catalyzed with a solid absorbent catalyst, or it may be a turbo-mixer or jet contactor type of reactor in the case of liquid catalysts. The reactor effluent flows by way of line 6 to stabilizer 7 where the excess hydrogen sulfide is taken overhead through line 8 to the hydrogen sulfide storage tank 9. The product stream now free of H2S is taken via line 9 to fractionator 10 where light mercaptans consisting mainly of lower boiling mercaptan compounds are drawn off through line 11 to storage. The kettle product from this operation which now comprises unreacted olefin and mercaptans with high molecular weight is withdrawn from the column through line 12 and is emulsified with controlled proportions of hydrogen peroxide from line 13 prior to injection into the oxidation reactor 14. Suitable means are supplied in the reactor 14 to maintain intimate dispersion of the oxidizing solution with the incoming mercaptan feed. The oxidizing solution is essentially an aqueous solution of cupric chloride together with HCl added in sufficient amount to keep the solution in the system the same as one of cupric chloride. The cupric chloride solution is fed to reactor 14 via line 25. During the passage of the organic phase through the oxidation zone, the combined action of cupric ions and hydrogen peroxide effect the conversion of the mercaptans to disulfides with substantially no change in composition of the oxidizing solution other than the diluent effect of water introduced with the peroxide. The hydrogen peroxide and mercaptan are added at such rates that in the continuous operation described the peroxide is entirely consumed as fast as it is added and therefore its concentration never builds up to any substantial extent in the reaction zone. The hydrogen peroxide does not react in the absence of cupric chloride. The hydrogen peroxide is converted to water as it is consumed. The emulsion of the product stream and copper solution is continuously removed from the reactor via line 15 to separator 16 where gravity separation of the product stream and copper solution takes place. The oxidized organic phase is continuously discharged through line 17 to vacuum fractionator 18 where unreacted high-boiling olefinic hydrocarbons constitute the overhead stream which is returned to olefin storage 1 through line 19. The product disulfides substantially free of mercaptan impurities are withdrawn from the fractionator through line 20.

The oxidation system is maintained at full strength as indicated in the drawing. The some-what dilute copper solution is removed from separator 16 through line 21. A portion or all of the stream may be diverted to evaporator zone 23 where the solution is concentrated with water vapor being discharged through line 24. The concentrated solution is recycled to the oxidation reactor 14 through line 28 along with dilute copper per solution from line 21, make-up copper solution from line 28 and replacement HCl from line 21. Addition of HCl is necessary because some is lost in the evaporation in unit 23 which tends to cause the cupric chloride solution to become basic preventing operation.

In the mercaptan-synthesis stage of this invention, catalytic reactions are especially desirable since the high molecular weight mercaptans specified herein are not sufficiently stable to withstand the high temperatures required in straight thermal processes. The reaction between the olefins and hydrogen sulfide may be effected in the presence of a variety of solid and liquid catalysts. Solid contact catalysts may include: silicas promoted with various metal oxides, metallic sulfldes, silica gel, Fuller's earth and charcoal. Liquid catalysts such as sulfuric acid, hydrogen fluoride and various complex compounds of boron fluoride may be used to promote the reaction.

A preferred solid contact catalyst is a gel-type material comprised essentially of silicas and a metal oxide selected from group IIIA or group IIIB of the periodic table with various quantities of water. Silica-alumina compositions represent specific types that may be employed to bring about a high conversion per pass at temperatures ranging from about 200° to about 300° F.

Among available liquid catalysts, anhydrous hydrogen fluoride and complex compounds of boron fluoride with phosphoric acid and water are preferred due to their high activity at low temperatures. With these catalysts under conditions of liquid-liquid contacting, mercaptan formation can be effected at temperatures ranging from about 32° to about 100° C.

The hydrocarbon feed for the present process is ordinarily confined to aliphatic olefins having from about 12 to about 16 carbon atoms per molecule. A convenient source of such material is the heavy polymer produced in catalytic codimer operation charging propylene and butylene.

General reaction conditions employed in the mercaptan stage include: (1) a molal excess of H2S with respect to olefin of about 1:1 to 1:5; (2) reaction pressures of 500 to about 2000 p.s.i. to maintain liquid or dense phase operation.

The oxidizing copper solution of the disulfide conversion stage comprises an aqueous solution of cupric copper in the presence of a chloride ion concentration equivalent to that of 10 to 20 weight per cent sodium chloride solution. The cupric copper concentration may vary from about 3 per cent to about 14 weight per cent although intermediate concentrations of from about 5 to 7 per cent are ordinarily preferred.

The hydrogen peroxide of the oxidizing system may vary in concentration from about 3 per cent to 30 per cent aqueous stabilized solutions. However, because of the considerable diluent effect on the copper solution and consequent load on the evaporators of the dilute solutions, the more concentrated reagents containing from 15 to 30 per cent H2O2 are preferred. Regardless of the strength of the peroxide solution, it is desirable to have a slight excess of H2O2 over that called for in a hypothetical direct stoichiometric oxidation of the mercaptan to disulfide. Thus 1.1 times the theoretical weight of H2O2 has been found adequate although higher concentrations obviously may be employed.

The volume ratio of copper solution to dry mer-
The process of preparing high molecular weight alkyl disulfides having the general formula \( \text{R-S-S-R} \) where \( \text{R} \) is an alkyl group having from 12 to 16 carbon atoms which comprises reacting a \( \text{C}_{12} \) to \( \text{C}_{16} \) olefin with hydrogen sulfide to form the corresponding alkyl mercaptan, removing unreacted hydrogen sulfide and mercaptans having less than 12 carbon atoms from the reaction mixture, subjecting the resulting reaction mixture containing the \( \text{C}_{12} \) to \( \text{C}_{16} \) alkyl mercaptan together with unreacted olefin to the simultaneous action of hydrogen peroxide and aqueous cupric chloride solution and thereby oxidizing the mercaptan content thereof to said disulfide, the unreacted olefin serving to minimize foaming and reduce viscosity during the oxidation, vacuum fractionating the unreacted olefin from said disulfide and recycling said unreacted olefin to said reacting step for further reaction with hydrogen sulfide, and recovering said disulfide as the product of the process.

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