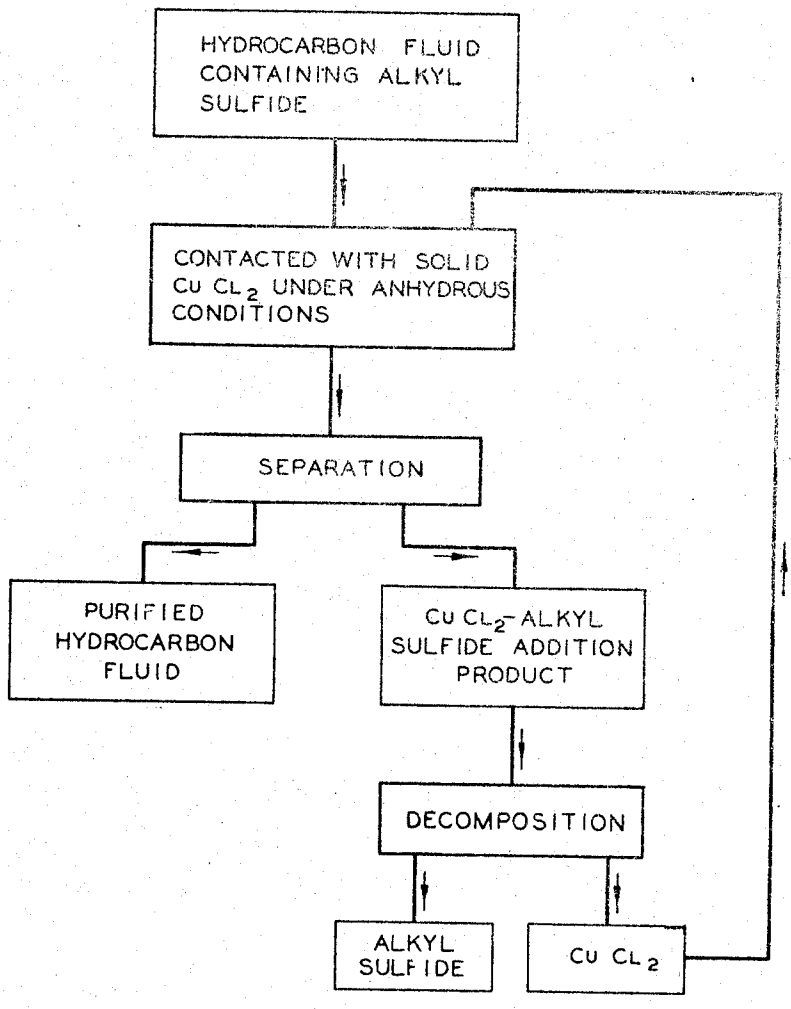
Nov. 7, 1944. W. A. SCHULZE ET AL 2,362,219

PRODUCTION OF ALKYL SULPHIDES

Filed Dec. 2, 1941



INVENTOR
W. A. SCHULZE
LLOYD C. MORRIS
BY Hudson, Young & Yinger
ATTORNEY

Patented Nov. 7, 1944

2,362,219

UNITED STATES PATENT OFFICE

2,362,219

PRODUCTION OF ALKYL SULPHIDES

Walter A. Schulze and Lloyd C. Morris, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

Application December 2, 1941, Serial No. 421,346

10 Claims. (Cl. 260—609)

The present invention relates to a process for the production of dialkyl monosulphides, hereinafter termed alkyl sulphides. More particularly, this invention relates to a process for the selective absorption of dialkyl monosulphides from low-boiling hydrocarbon fluids or from dilute solutions in other similarly inert solvents, and to the subsequent recovery and/or purification of the alkyl sulphides.

This application is a continuation-in-part of our co-pending application, Serial No. 318,648 filed February 12, 1940, Patent 2,271,665. The patent relates to a process for removing alkyl sulphides from sweet hydrocarbon fluids by treatment with solid, anhydrous cupric chloride, or carrier impregnated anhydrous cupric chloride. The present application is directed to the removal of the sulphonium addition compound formed from the anhydrous reagent and treatment for the recovery of valuable concentrated alkyl sulphide.

The alkyl sulphides of the general formula R—S—R' where R and R' represent alkyl groups occur naturally in petroleum oils and related products as one of a group of relatively common sulphur impurities which also includes hydrogen sulphide, mercaptans and dialkyl disulphides. While the origin of the alkyl sulphides is obscure, they may be formed during various processing steps applied to petroleum by the reaction of olefins with hydrogen sulphide or by the thermal decomposition or partial oxidation of mercaptans. Thus, while alkyl sulphides may be prepared by other means and from other sources, the most abundant supply is provided in petroleum distillates.

The alkyl sulphides have boiling points intermediate with respect to the corresponding mercaptans of formula R—SH and the corresponding dialkyl disulphides of the formula R—S—S—R'. Moreover, alkyl sulphides are resistant to further oxidation: for example, such strong oxidizing agents as alkaline permanganate solutions are required to form the corresponding sulphoxides and sulphones. For this reason, alkyl sulphides are relatively stable and are not affected by the reagents of the type used to oxidize mercaptans to disulphides. The alkyl sulphides also have the tendency to form azeotropic mixtures with lower boiling hydrocarbons, and therefore appear in relatively large concentrations in hydrocarbon fractions from which removal and/or recovery by fractionation alone is not feasible. Hence, in view of the unreactive nature of the compounds and the difficulties attending segregation, the recovery of alkyl sulphides from complex hydrocarbon mixtures has not heretofore been practiced.

The principal object of this invention is to provide a process for the separation of alkyl sulphides from dilute solutions in hydrocarbons or similar solvents. A further object of this invention is to provide a process for the subsequent recovery of said alkyl sulphides in concentrated form. As will be disclosed hereinafter, our process serves a dual purpose in both separating the alkyl sulphides from hydrocarbon fluids and in also providing a means for the manufacture of alkyl sulphide concentrates suitable for the production of complex organic sulphur compounds, the odorization of natural gas and various other useful purposes. For example, ethyl sulphide may be chlorinated substitutively to give dichlorodiethyl sulphide (mustard gas) which is a valuable war material and synthetic intermediate.

The accompanying drawing portrays a flow diagram of the process of the present invention.

We have discovered that when hydrocarbon fluids containing alkyl sulphides and substantially free of hydrogen sulphide and mercaptans are brought into contact with solid anhydrous cupric chloride reagents in the substantial absence of water, the alkyl sulphides are selectively absorbed and retained by the cupric chloride reagent. The reagent bearing alkyl sulphides is then treated in any suitable way to decompose the alkyl sulphide-cupric chloride addition products, as by heating to moderate temperatures, whereby the alkyl sulphides are released and the reagent is simultaneously reactivated for further use in the absorption step. The desorbed alkyl sulphides may be collected by suitable means and used as obtained or further purified by fractionation if desired.

We have noted that when solutions of alkyl sulphides in hydrocarbon fluids are subjected to a relatively brief contact-type treatment with substantially anhydrous solid cupric chloride in the substantially complete absence of water, including water of crystallization, that the alkyl sulphides react to form a type of addition compound which is insoluble in hydrocarbon fluids. The exact reaction thus occurring is not known but it is suggested, without thereby limiting our invention, that this reaction takes place:

$$\underset{\text{Alkyl sulphide}}{R—S—R'} + \underset{\text{Cupric chloride}}{CuCl_2} \rightarrow \underset{\text{Sulphonium addition compound}}{RR'—S—CuCl_2}$$

This projected formation of an addition compound is based on the fact that anhydrous conditions are necessary for the reaction, and that chloride ions are not substantially displaced by the reaction. Further, the spent cupric chloride reagent may be quickly and completely regenerated by heating gently at atmospheric or subatmospheric pressure.

In one specific application, our process comprises the passage of a hydrogen sulphide-free doctor-sweet hydrocarbon fluid containing alkyl sulphides through a bed of solid anhydrous cupric chloride reagent at atmospheric temperatures and flow rates favoring substantially complete conversion of the alkyl sulphides to cupric chloride addition compounds. The unreacted hydrocarbons are then removed as completely as possible from the reagent space, and the reagent bed is heated to temperatures which cause the decomposition of the addition compound and the evolution of the alkyl sulphides. The latter are then recovered in the form of a concentrate whose purity varies with the completeness of removal of hydrocarbons prior to desorption.

Since the reaction forming the alkyl sulphide addition compound requires a substantially anhydrous cupric chloride reagent, the absorption step is conducted under substantially anhydrous conditions. The hydrocarbon fluids to be treated are, therefore, freed of entrained water and may be dehydrated to remove dissolved water by means of conventional dehydration treatments, preferably utilizing the more efficient desiccants such as activated alumina, activated bauxite, silica gel and the like.

Dialkyl disulphides do not react with our anhydrous cupric chloride reagent, but hydrogen sulphide and mercaptans will react therewith forming metal sulphide and dialkyl disulphides, respectively. Thus hydrogen sulphide and mercaptans should be absent from the solutions being treated by our process to avoid spending the reagent. The cupric chloride converted to cupric sulphide by hydrogen sulphide and that converted to cuprous chloride by oxidation of mercaptans to dialkyl disulphides is not regenerated by our process and hence presence of these substances destroys the reagent for the present purpose.

The alkyl sulphide can be recovered quickly by heating the sulphonium addition product to decomposition temperatures which may range from about 150° F. to about 250° F. The regeneration may be completed more rapidly by passing an inert gas at an elevated temperature through the reagent bed during the regeneration. This stream of gas containing the desorbed alkyl sulfide is then passed through a condenser and/or separator in which the alkyl sulphide is condensed, while the non-condensible inert gas is either vented or recycled as desired.

The cupric chloride reagents, useful in our process, may be the solid compound alone in suitable particle size, or the reagent prepared by impregnating a solid adsorbent carrier material with cupric chloride solutions in water, and subsequent drying of the impregnated material to substantially anhydrous form, which entails the removal of water of solution and water of crystallization. Or, the anhydrous cupric chloride may be intimately mixed with an anhydrous carrier material to obtain greater dispersion and active surface for the reagent. We have found that superior physical properties affecting the contact of reagent with hydrocarbon fluid may be obtained by the use of our carrier-impregnated anhydrous reagent.

The process is not limited to the use of anhydrous cupric chloride as such, since an active reagent may be prepared by impregnating an inert carrier material with a water solution of salts which furnish the requisite cupric and chloride ions. For example, in the preparation of one cupric chloride reagent we may use a solution containing cupric sulphate or acetate and a chloride of the alkali or alkaline-earth metals, or of ammonium, zinc, magnesium or aluminum. Such impregnated reagents when dried to a substantially anhydrous condition are active in the removal of alkyl sulphides from hydrocarbon oils.

The following examples are included to further illustrate the operation of our process without implying thereby any limitation on our invention.

Example 1

A pentane fraction manufactured at a natural-gasoline plant was found to contain hydrogen sulphide, mercaptans, and alkyl sulphides. This stock was caustic washed, sweetened, and refractionated to remove disulphides resulting from the sweetening process. Analysis then showed a sulphur content of 0.01 weight per cent of alkyl sulphides which, on account of the hydrocarbon boiling range, was almost entirely methyl sulphide. The methyl sulphide was removed by percolating the dehydrated hydrocarbon liquid at atmospheric temperature through an anhydrous reagent prepared by impregnating fuller's earth with cupric chloride solution and subsequent complete drying. Five hundred liquid volumes of charge stock were passed over one volume of the reagent. At the beginning of the experiment, the treated pentane contained 0.0002 weight per cent of sulphur, indicating substantially complete removal of methyl sulphide, while at the end 90 per cent removal was being accomplished. The reagent bed was freed of pentanes by flushing with methane at atmospheric temperature. The temperature of the reagent bed was then raised to 200° F. by passing hot methane through it. The heating was continued until the bed was freed of methyl sulphide. The hot methane after passage through the tower was cooled and taken through a condenser and separator in which the methyl sulphide was condensed and separated. The stripped methane was then reheated and returned through the reagent bed. The recovered methyl sulphide concentrate without further purification was 95 per cent pure.

Example 2

A doctor-sweet, hydrogen-sulphide-free liquid hydrocarbon mixture containing mainly hexanes and heptanes was analyzed and found to contain 0.02 weight per cent of sulphur as alkyl sulphides and disulphides. This stock was then passed in the absence of water and at a temperature in the range of 70 to 80° F. over a reagent prepared by impregnating fuller's earth with a solution of cupric sulphate and sodium chloride and drying to substantially anhydrous state. The hydrocarbon mixture after this treatment had a sulphur content of 0.005 weight per cent, indicating substantially complete removal of all the alkyl sulphides present in the original material. When the reagent became saturated with respect to alkyl sulphides it was regenerated

as in Example 1, collecting the desorbed alkyl sulphides as a concentrate containing ethyl and methylethyl sulphides.

Example 3

A low end-point straight-run gasoline from a refinery processing operation was sweetened and passed at a temperature of 80° F. and a flow rate of one liquid volume per hour per volume of reagent over a bed of anhydrous cupric chloride on bauxite. When calculations based on the initial sulphur reduction showed apparent saturation of the reagent with alkyl sulphides, gasoline was drained from the bed, and sulphur-free fuel gas was passed through at 80 to 90° F. to assist in purging hydrocarbons from the reagent space. The reagent bed was then heated to a temperature of 250° F. with hot gas, and alkyl sulphides were condensed and separated from the gas stream. Fractionation of the recovered material showed a high percentage of methyl, ethyl and diisopropyl sulphides with smaller amounts of di-n-propyl and dibutyl sulphides. These materials were concentrated by the fractionation into concentrates of 50 to 90 per cent purity, with the methyl sulphide obtained in purest form.

The temperatures of the alkyl sulphide absorption step using our process are ordinarily atmospheric temperatures between 30° and 110° F. Higher temperatures may be used, but such temperatures tend to favor the reversal of the removal reaction. The pressures during this step may vary from atmospheric to super-atmospheric pressures ranging between 15 and 500 pounds per square inch. The operating pressure may depend on the nature of the fluid being treated. For example, in treating normally gaseous fluids such as propane and butane in liquid phase, sufficient pressure is provided to avoid vaporization. We usually prefer to treat in liquid phase since the volume of reagent required for nominal flow-rates, say 0.5 to 10 volumes per hour per volume of reagent, is not excessive. However, treating in gaseous or vapor phase is entirely satisfactory with normally gaseous hydrocarbons, providing due allowance for contact time is made in the size of the reagent bed.

The desorption and recovery of alkyl sulphides from the absorption reagent may be carried out at moderate temperatures in the range of 150 to 250° F. at atmospheric or subatmospheric or superatmospheric pressures. The use of subatmospheric pressures enables the use of lower temperatures in the above-named range, but we ordinarily prefer to use higher temperatures of 200 to 250° F. with at least atmospheric pressures on the system used for recovering the desorbed sulphide.

Since the purity of the desorbed material depends on the extent to which hydrocarbons are removed from the reagent prior to heating to desorption temperatures, a variety of procedures may be employed to aid in the preparation of a purer product without subsequent fractionation or other treatment. With lower-boiling hydrocarbons, such as C_4 and C_5 hydrocarbon mixtures, vaporization of the unreacted material in the reagent space is often satisfactory and involves no loss of alkyl sulphides. With higher-boiling liquids, drainage of the liquid from the reagent, followed by purging with a suitable low-boiling liquid and/or gas may be practiced. In case the presence of the hydrocarbons does not interfere with utilization of the alkyl sulphide concentrates, such procedures may be omitted.

The foregoing disclosure and examples are to be taken as illustrative and not as limitative of our invention, the scope of which is limited only by the following claims.

We claim:

1. The process which comprises thermally decomposing an addition compound of an alkyl monosulphide and cupric chloride at an elevated temperature sufficiently high to liberate the alkyl monosulphide therefrom.

2. The process which comprises decomposing an addition compound of an alkyl monosulphide and cupric chloride by heating said compound at a temperature within the range of approximately 150° to approximately 250° F. to liberate the alkyl monosulphide therefrom.

3. The process which comprises decomposing an addition compound of an alkyl monosulphide and cupric chloride while passing an inert gas thereover at an elevated temperature sufficiently high to liberate the alkyl monosulphide therefrom.

4. The process which comprises decomposing an addition compound of cupric chloride and an alkyl monosulphide having not more than four carbon atoms in either alkyl radical thereof by heating said compound at a temperature within the range of approximately 150° to approximately 250° F. to liberate the alkyl monosulphide therefrom.

5. The process which comprises contacting an alkyl monosulphide with substantially anhydrous cupric chloride under substantially anhydrous conditions to form an addition compound of the alkyl monosulphide and cupric chloride and thereafter thermally decomposing said addition compound at an elevated temperature sufficiently high to liberate said alkyl monosulphide and regenerate said cupric chloride.

6. The process which comprises contacting an alkyl monosulphide with substantially anhydrous cupric chloride under substantially anhydrous conditions to form an addition compound of the alkyl monosulphide and cupric chloride and thereafter decomposing said addition compound by heating it to a temperature within the range of approximately 150° F. to approximately 250° F. to liberate said alkyl monosulphide and regenerate said cupric chloride.

7. The process for the recovery of an alkyl monosulphide from a solution thereof in an inert solvent which is substantially free from other sulphur compounds, which comprises contacting said solution with a reagent comprising a substantial proportion of substantially anhydrous cupric chloride under substantially anhydrous conditions to form an insoluble addition compound of the alkyl monosulphide and cupric chloride, separating the reagent comprising said addition compound from the treated liquid and recovering the alkyl monosulphide therefrom in concentrated form by heating said reagent at an elevated temperature sufficiently high to liberate the alkyl monosulphide therefrom.

8. The process for the recovery of an alkyl monosulphide from a hydrocarbon liquid containing the same that is substantially free from other sulphur compounds, which comprises contacting said liquid under substantially anhydrous conditions with a reagent comprising substantially anhydrous cupric chloride to form an insoluble addition compound of the alkyl monosulphide and cupric chloride, separating the reagent comprising said addition compound from the treated liquid and recovering the alkyl mono-

sulphide therefrom in concentrated form by heating said reagent at an elevated temperature sufficiently high to liberate the alkyl monosulphide therefrom.

9. The process for the recovery of an alkyl monosulphide having not more than four carbon atoms in either alkyl radical thereof from a solution thereof in an inert solvent which is substantially free from other sulphur compounds, which comprises contacting said solution with a reagent comprising a substantial proportion of substantially anhydrous cupric chloride under substantially anhydrous conditions to form an insoluble addition compound of the alkyl monosulphide and cupric chloride, separating the reagent comprising said addition compound from the treated liquid and recovering the alkyl monosulphide therefrom in concentrated form by heating said reagent at a temperature within the range of approximately 150° to approximately 250° F. to liberate the alkyl monosulphide therefrom.

10. The process for the recovery of an alkyl monosulphide from a substantially anhydrous, doctor-sweet petroleum hydrocarbon liquid that is substantially free from hydrogen sulphide and that contains an alkyl monosulphide, which comprises contacting said petroleum hydrocarbon liquid with a reagent comprising a substantial proportion of substantially anhydrous cupric chloride to form an addition compound of the alkyl monosulphide and cupric chloride, separating the reagent comprising said addition compound from the treated liquid and recovering the alkyl monosulphide therefrom in concentrated form by heating said reagent at a temperature within the range of approximately 150° to approximately 250° F. to liberate the alkyl monosulphide therefrom.

WALTER A. SCHULZE.
LLOYD C. MORRIS.