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PROCESS FOR THE REMOVAL OF CARBONYL SULFIDE FROM A HYDROCARBON FLUID

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1

This invention relates to an improved process for the conversion of carbonyl sulfide, particularly the hydrolysis of carbonyl sulfide, in the presence of an alkali. More particularly the invention relates to a process of treating fluid mixtures containing carbonyl sulfide to effect its ready separation therefrom. The process of this invention is especially applicable to the treatment of hydrogen-containing gaseous mixtures obtained by the reaction of steam with hydrocarbons and/or coke, and the treatment of hydrocarbon fluids resulting from the thermal cracking of crude petroleum oils.

Hydrocarbon fluids such as those obtained from crude petroleum oils and other sources usually contain varying amounts of deleterious sulfur compounds. The kinds and amounts of sulfur compounds occurring in any hydrocarbon fluid vary with the source material and with the method of manufacturing and processing of said fluid.

Many of the sulfur compounds present in hydrocarbon fluids are detrimental to the processing or marketing of said fluids or of products derivable therefrom. Hydrogen sulfide and its alkyl derivatives, the mercaptans, are particularly objectionable in petroleum fluids. Methods have been developed for removing hydrogen sulfide and mercaptans from such fluids based, for the most part, upon their acidic properties and also upon the insolubility of certain metallic sulfides.

Carbonyl sulfide represents another form in which sulfur usually exists in some petroleum fluids, particularly the lower boiling hydrocarbon fractions such as C_3–C_4 fraction from refinery gases. Carbonyl sulfide has a low boiling point in the order of that of propane. Consequently, it cannot be readily separated therefrom by fractionation. Furthermore, it is relatively stable toward acidic reagents, and is only slowly affected by strongly alkaline treating reagents such as solutions of caustic soda and the like. Thus, its removal is not effected satisfactorily by the use of strongly alkaline solutions which are utilized for the removal of hydrogen sulfide, mercaptans and the like.

An object of the present invention is to provide a novel and economical process for the removal of carbonyl sulfide from organic compounds or compositions containing it. Another object of this invention is to provide a more complete

2

desulfurization of cracked hydrocarbon fractions of lower molecular weight hydrocarbons which desulfurization is preferably effected after conventional methods for the removal of hydrogen sulfide and mercaptans have been applied.

Heretofore, it has been proposed to remove carbonyl sulfide from petroleum fluids by methods involving oxidation in the presence of activated charcoal impregnated with alkali, treatment with derivatives of alkyl amines such as the alkylolamines, and for conversion to insoluble metallic sulfides by contacting with a carrier impregnated with compounds of metals such as lead, copper and cadmium in the presence of an alkaline reagent. However, none of these methods is entirely satisfactory. In the oxidation of sulfides free sulfur is normally among the products of oxidation and it is particularly difficult to remove it from the fluid mixture being treated. Furthermore, the addition of oxygen or an oxygen-containing gas, e. g. air, to a mixture of hydrocarbons is undesirable because of the danger of forming an explosive mixture; also unsaturated hydrocarbons present may be partially oxidized to undesirable products. The use of alkylolamines is economically unsatisfactory except when by-products resulting therefrom are of sufficient value to absorb a portion of the cost of the amines. The solid or supported treating materials such as fuller's earth impregnated with an alkali together with sodium plumbite or a copper or a cadmium salt possesses the usual disadvantage of requiring complete cleaning and refilling of the treating chamber or tower with fresh solid material at spaced time intervals whereas in the use of a fluid treating agent replacement or fortification may be carried out substantially continuously.

As stated hereinabove, it has been known that carbonyl sulfide reacts slowly with alkaline solutions such as caustic soda. This reaction of carbonyl sulfide is substantially an hydrolysis, presumably first into a salt of thiacarbonic acid and finally to yield salts of carbonic acid (carbon dioxide) and of hydrosulfuric acid (hydrogen sulfide). The net result may be represented by the equation $COS+H_2O=CO_2+H_2S$. In the presence of the alkali the acids are converted into their respective salts which are very soluble in

water and thus retained in the aqueous treating solution.

Now, in accordance with the present invention an improved process has been discovered for effectively and economically hydrolyzing carbonyl sulfide and for removing it from fluid mixtures containing it.

Broadly stated, in the improved process of this invention, the carbonyl sulfide, or a fluid e. g. gaseous mixture containing it is treated with an alkaline reagent in the presence of a metal salt of an oxide of an amphoteric element which element does not form an acid-insoluble metallic sulfide.

In carrying out the process of this invention in accordance with a preferred embodiment thereof, a fluid mixture such as a mixture of light hydrocarbons occurring in a C_3–C_4 fraction produced by cracking a petroleum oil, and which mixture contains carbonyl sulfide, is first treated to remove hydrogen sulfide and mercaptans by a suitable conventional method, and the resulting mixture is then contacted, such as by countercurrent flow, with an alkaline solution, e. g., a caustic soda solution, containing aluminum oxide (hydroxide) dissolved therein as sodium aluminate ($NaAlO_2$). The carbonyl sulfide is effectively removed from the hydrocarbons by the alkaline solution containing the aluminate salt. The resulting fluid mixture may be treated then by any suitable well known method to remove the moisture, such as by contacting with activated alumina, calcium chloride, etc.

In addition to the effective removal of the carbonyl sulfide from the light cracked hydrocarbon fraction by contacting the same with an alkaline solution of an aluminate, the treatment effects a marked reduction in the gum and/or non-volatile matter content of the hydrocarbon fraction. A reduction of 85% in the initial gum content is readily effected.

The removal of carbonyl sulfide from fluid mixtures by the process described above represents a marked improvement over processes wherein said mixture is contacted successively with an alkali and with aluminum oxide, or with either one alone. Thus, in accordance with the present invention, the reaction (hydrolysis) of carbonyl sulfide when contacted with an alkaline solution is accelerated in the presence of a salt such as sodium aluminate. It appears therefore that the aluminate ion (AlO_2^-) catalyzes the hydrolysis of the carbonyl sulfide. Although the mechanisms involved in the transformations which take place are not known, the accelerating effect of the metallic element, e. g., aluminum, may be accounted for on the basis of the bonding force between aluminum and sulfur. The bonding strength between aluminum and sulfur is relatively weak as indicated by the fact that aluminum sulfide is relatively unstable in water, hydrolyzing to aluminum hydroxide and hydrogen sulfide. This is somewhat analogous to the behaviour of aluminum hydroxide in acidic and in basic solutions; in an acidic solution there is a cleavage between aluminum and oxygen atoms, whereas, in a basic solution there is a cleavage between oxygen and hydrogen. That is, aluminum hydroxide may be considered as both a proton donor and a proton acceptor, hence an amphoteric substance. Thus aluminum is an amphoteric element.

In accordance with this theory, which, of course, is to be construed only as a theory of a portion of the mechanism involved in the process of the present invention and is not to be construed as a limitation to the invention, the amphoteric element probably forms a linkage with the sulfur atom of the carbonyl sulfide at one stage of the reaction, and is severed therefrom at a subsequent stage, possibly releasing the sulfur as a sulfide ion.

In the process of this invention the accelerating substance, such as the sodium aluminate (or aluminate ion), is not consumed. Only the alkali is consumed as in the case of the usual hydrolysis of carbonyl sulfide in an alkaline medium. Since the purpose of the alkali is to maintain alkaline conditions and to neutralize the carbonic acid and hydrogen sulfide as formed, the concentration of alkali may be varied within wide limits. Also, many different substances may be utilized to maintain the alkalinity of the treating solution, as will be well understood in the art. For example, alkali metal hydroxides and oxides (not peroxides) and salts of relatively weak acids, particularly salts which hydrolyze to give alkaline solutions, such as sodium and potassium carbonates, tertiary sodium and potassium orthophosphates, may be used. Hydroxides and oxides of alkaline earth metals, such as those of magnesium and calcium may be utilized if desired. In place of the usual inorganic alkaline substances, organic bases such as amines, quarternary ammonium compounds, and the like, may also be employed.

The invention has been described with reference to the use of sodium aluminate as the accelerating agent for the hydrolysis of carbonyl sulfide in an alkaline solution. It will be understood, of course, that the aluminate will generally be formed in the treating solution by adding an aluminum salt, such as aluminum sulfate or aluminum chloride, to the alkaline solution, the aluminum salt reacting with the alkali to form the aluminate. It has been discovered also, in accordance with this invention, that there are other elements which exert an accelerating action similar to that of aluminum in the process under discussion. In general, other suitable elements are those whose oxides are amphoteric and which do not form sulfides insoluble in dilute acid solutions, i. e., whose sulfides are soluble in dilute acid solutions, such as, e. g. 0.3N HCl solution. Zinc and chromium are examples of such elements. Thus, sodium zincate (Na_2ZnO_2), sodium chromite ($NaCrO_2$), and other analogous zincates and chromites may be used in the process of this invention.

The conditions under which the accelerated hydrolysis by the process of this invention may be carried out may be varied within wide limits. For example, the process may be performed as a gaseous-liquid or a liquid-liquid phase operation. It will be appreciated, however, that since the volume of fluid to be treated for a given size plant installation will be smaller when the fluid is in a liquid state than when it is gaseous, it will generally be preferred to maintain the fluid in the liquid state by suitable temperature and pressure adjustments, if necessary. The process may be batch-wise with usual agitation as in a closed container, or it may be operated intermittently or continuously as in a packed tower or a tower provided with bubble caps and the like.

It has been found that in general dilute caustic solutions are more efficacious than very strong solutions. Solutions with strengths ranging up to about 7° Baumé caustic have been found to be particularly effective.

The amount or concentration of the acceler-

ating agent, e. g., sodium aluminate, which will be used will depend upon a number of variable factors, such as the temperature, concentration of alkali, time of contact, etc. The optimum quantity may be determined in any particular case by experiment in view of the present invention. A concentration of from about 0.6 to about 1.2 grams of sodium aluminate or molecular equivalent of sodium chromite or sodium zincate when dissolved in 100 grams of a 5° Baumé caustic solution in water has been found to be especially effective for removing minor amounts of carbonyl sulfide from fractions of light hydrocarbons produced by high temperature cracking of petroleum oil or distillates thereof.

An advantage of this invention over prior art methods of removing carbonyl sulfide from fluid mixtures is that hydrogen sulfide and mercaptans need not be removed prior to the step for removing the carbonyl sulfide, since the same material, namely caustic soda, is used for eventually removing all three substances. For reasons of operation it may be desirable in some cases to remove the hydrogen sulfide and mercaptans prior to removal of the carbonyl sulfide while in other cases simultaneous removal of all the substances may be preferred.

The following examples representing preferred embodiments of the invention will serve to illustrate a method of practicing the invention:

Example I

Liquefied residual propane, recovered from the alkylation of benzene with propylene which latter had previously been produced by dehydration of a mixture of low-boiling petroleum hydrocarbons, was intimately contacted at 75° F. for 10 to 15 minutes with about one-sixth of its own volume of an aqueous caustic soda solution of 5° Baumé strength containing 0.8 gram of $NaAlO_2$ per 100 grams of solution. At a flow rate of 2,000 barrels of propane per day the removal of carbonyl sulfide was 85–90% of the initial content of 0.03 gram COS per 100 cc. of liquid residual propane.

Example II

When a butane fraction of cracked petroleum hydrocarbons containing about 0.025 gram of COS per 100 cc. of liquid fraction is agitated at 75° F. for 10–15 minutes with about one-fifth of its own volume of an aqueous caustic soda solution of 5° Baumé strength and containing about 1.0 gram of sodium chromite ($NaCrO_2$) per 100 grams of solution, the removal of the carbonyl sulfide is found to be substantially complete.

The improved process of hydrolyzing carbonyl sulfide in accordance with this invention is of utility in many processes involving the use of different fluid substances. In the synthesis of ketones such as acetone by the catalytic dehydrogenation of secondary alcohols such as isopropyl alcohol which has been prepared from propylene obtained from cracked refinery gases, it is very important that sulfur compounds such as carbonyl sulfide are removed from the reactants to prolong the effective life of the dehydrogenation catalyst. The unsaturated hydrocarbons obtained from cracked petroleum oils and used for alkylations, polymerizations, hydrations, and the like may be effectively purified of carbonyl sulfide by utilizing the process of this invention. Furthermore, hydrocarbon mixtures containing unsaturated substances such as olefins and the like, and which mixtures contain gums and resin compounds such as are formed from polymerization

and/or oxidation of olefins, are advantageously treated by the process of this invention to effect the removal of such gums and resin compounds. Thus, hydrocarbon fractions containing high percentages of unsaturates, and which are subject to deterioration by gum formation, may be purified of gums by the process of the present invention. Carbonyl sulfide is often an undesirable constituent of hydrogen and carbon monoxide mixtures prepared by employing the water gas reaction or the reaction of steam with hydrocarbons at an elevated temperature. Hydrogen and hydrogen-nitrogen mixtures to be used in ammonia synthesis, where the hydrogen is obtained by steam cracking of petroleum hydrocarbons, including natural gas, may be advantageously purified of deleterious sulfur compounds, such as carbonyl sulfide, by practicing this invention.

We claim as our invention:

1. A process for the removal of carbonyl sulfide from a hydrocarbon fluid containing carbonyl sulfide which comprises contacting said fluid with an aqueous alkaline solution in the presence of sodium aluminate.

2. A process for the removal of carbonyl sulfide from a hydrocarbon fluid containing carbonyl sulfide which comprises contacting said fluid with an aqueous alkaline solution in the presence of an alkali metal aluminate.

3. A process for the removal of carbonyl sulfide from a hydrocarbon fluid containing carbonyl sulfide which comprises contacting said fluid with an aqueous solution of an alkali metal hydroxide and an alkali metal aluminate.

4. A process for the removal of carbonyl sulfide from a hydrocarbon fluid containing carbonyl sulfide which comprises contacting said fluid with an aqueous solution of sodium hydroxide and sodium aluminate.

5. A process for the removal of carbonyl sulfide from a hydrocarbon fluid mixture containing carbonyl sulfide which comprises contacting said hydrocarbon fluid mixture with a solution consisting essentially of water, a water-soluble alkaline compound and a water-soluble salt of an anion selected from aluminate, zincate, chromite and mixtures thereof.

6. A process for the removal of carbonyl sulfide from a fluid mixture containing carbonyl sulfide admixed with a fluid substance which is insoluble in aqueous alkaline solutions and which it is desired to obtain in a purified form, which comprises contacting said fluid mixture with a solution consisting essentially of water, a water-soluble alkaline compound and a water-soluble salt of an anion selected from aluminate, zincate, chromite and mixtures thereof.

7. A process for the removal of carbonyl sulfide from a hydrocarbon fluid mixture containing carbonyl sulfide and which is substantially free from hydrogen sulfide and mercaptans, which process comprises contacting said hydrocarbon fluid mixture with an aqueous alkaline solution containing dissolved therein an alkali metal salt of an anion selected from aluminate, zincate, chromite and mixtures thereof.

8. A process for the removal of carbonyl sulfide from a fluid mixture which is free from hydrogen sulfide and mercaptans and which contains carbonyl sulfide admixed with a fluid substance which is insoluble in aqueous alkaline solutions and which it is desired to obtain in a purified form, which process comprises contacting said fluid mixture with an aqueous alkaline solution containing dissolved therein an alkali metal salt

of an anion selected from aluminate, zincate, chromite and mixtures thereof.

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