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PROCESS FOR THE OXIDATION OF MERCAPTIDES

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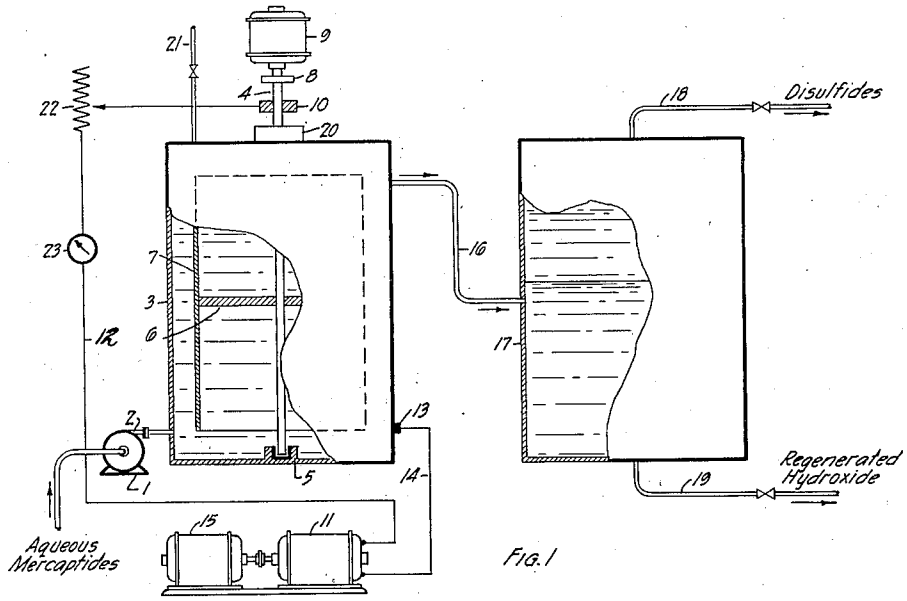


FIG. 1

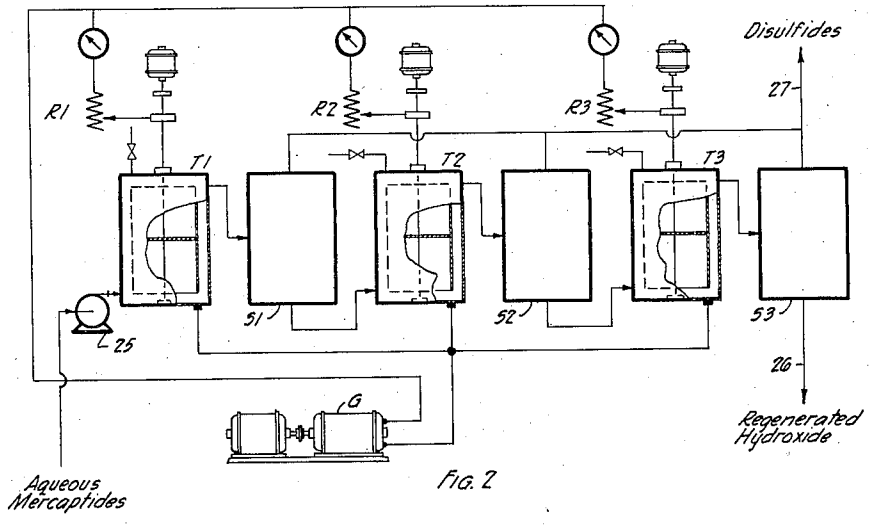


FIG. 2

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PROCESS FOR THE OXIDATION OF MERCAPTIDES

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8 Claims. (Cl. 204—9)

This invention relates to the electrolytic oxidation of mercaptides to disulfides in aqueous alkaline reacting solutions.

In the desulfurization of hydrocarbon oils large quantities of alkali hydroxides or other alkaline reacting hydroxides are used for the extraction of mercaptans. The disposal of the resulting obnoxious mercaptide solutions as well as the high consumption of treating chemicals make regeneration of the hydroxides without the use of additional chemicals very desirable.

It is the purpose of this invention to provide a practical method whereby spent aqueous alkaline reacting hydroxides containing mercaptides can be regenerated and mercaptides can be removed therefrom without the use of additional chemicals.

Our method consists essentially of electrolyzing an aqueous solution of mercaptides in a suitable electrolytic cell under conditions to oxidize the mercaptides to disulfides and to avoid substantially their oxidation to sulfonates.

Our process may be readily understood from a description of the attached drawing. Figure 1 represents a diagrammatic view of a single stage apparatus which in practice has given good results. Figure 2 shows a multistage apparatus consisting essentially of several treating units of the type shown in Figure 1. Referring to Figure 1, an aqueous solution of mercaptides is conveyed by pump 1 in line 2 into a cylindrical treating vessel 3. Rotatable shaft 4 is axially disposed in vessel 3, resting in insulated bearing 5 on the bottom plate of vessel 3. Attached to the shaft 4 by means of brackets 6 is concentrically arranged a perforated rotor 7. Shaft 4 extends upward through insulated stuffing box 20 on top of vessel 3 and is connected by means of an electrical insulator 8 to motor 9 which is preferably of the variable speed type. Vent 21 on top of vessel 3 serves for the escape of hydrogen produced on the cathode during the treatment.

The apparatus is supplied with a direct electric current from a 2 to 4 volt generator 11. The current passes through wire 12, ammeter 23, and variable resistance 22, which serve to measure and to control the current strength. The current then passes through electric brush 10 attached to shaft 4, through shaft 4, bracket 6, rotor 7, through the electrolyte in cell 3, through contact 13 attached to cell 3, through wire 14 back to generator 11. Rotor 7 may be either anode or cathode. Since it is desirable that the anode has as large a surface as possible for reasons hereinafter explained, we generally prefer to use rotor for the anode.

While the aqueous alkali mercaptide solution passes through vessel 3 a portion of the mercaptide is converted to disulfides. The resulting mixture passes through transfer line 16 to settling tank 17, where the disulfides are allowed to separate and rise to the top, to be withdrawn through line 18, while an aqueous hydroxide which is at least partly regenerated, leaves through line 19.

The electrodes, i. e. vessel 3 and rotor 7, may be constructed of any material of good electrical conductivity, which is resistant to the action of the aqueous hydroxide, and in the case of the anode, is also resistant to oxidation. The following materials have proven to be satisfactory: gold, silver, the platinum metals, iron, cobalt, nickel, stainless steels and other ferrous alloys, graphite and carbon. Lead and lead oxides are easily attacked by aqueous alkali hydroxide but may be used under some circumstances. Stainless steels, and particularly the alloy known as KA 2 metal, are very satisfactory. They are highly resistant to caustic at temperatures below about 100° C., strong, relatively cheap, and are preferentially wetted by aqueous hydroxide, rather than by the disulfides formed in the process. Graphite and carbon, while often useful, have the advantage of being brittle and tending to crumble, thereby contaminating the aqueous hydroxide.

Figure 2 shows 3 units of the type described in connection with Figure 1, arranged in series with respect to the flow of the aqueous hydroxide, which is pumped by pump 25 successively through treating vessels and settlers T1, S1, T2, S2, T3, S3. Regenerated aqueous hydroxide is withdrawn through line 26 while disulfides from the several treatments are collected in manifold 27. With respect to the electric current generated by the direct current generator G, the treaters T1, T2, and T3 are arranged in parallel. In order to enable the regulation of the current density through each treater individually, so as to maintain optimum treating conditions in each treater in spite of the changing composition of the aqueous hydroxide from treater to treater, each circuit is equipped with individual variable resistance, R1, R2, and R3, respectively.

While we have described in the foregoing a particular type of cylindrical electrolytic cell, containing a rotatable cylindrical anode, it shall be understood that other forms of cells are suitable as well. A type of cell which is frequently

used in electrolysis, comprising a series of alternating positive and negative electrode plates in a rectangular cell, has also given satisfactory results.

Our process is applicable to any aqueous solution of mercaptide and is particularly useful when applied to the mercaptide solutions obtained in the treatment of petroleum oils with aqueous alkaline reacting hydroxides. The term "alkaline reacting hydroxides", as used in this specification, is meant to apply to hydroxides which are capable of extracting mercaptans from their non-aqueous solutions by forming water soluble mercaptides and includes the alkali metal hydroxides, alkali earth hydroxides, and quaternary ammonium bases. The concentration of the mercaptide solutions, which are susceptible to our treatment, may vary within wide limits, the only requirement being that they be liquid.

Normally solid aqueous alkali hydroxides containing mercaptides and from 2–50% water may be subjected to our process at temperatures sufficiently high to liquefy them.

The treatment may be carried out advantageously at temperatures between about 0° and 100° C. and preferably between 20° and 60° C. although higher or lower temperatures may be employed. At relatively low temperatures below about 0° C. undesirable side reactions such as the formation of sulfonic acid tend to proceed at harmful rates; and at high temperatures in excess of about 100° C. many electrode materials, which at lower temperatures are suitable and resistant to the combined action of caustic and oxygen, are severely attacked and corroded. To avoid undue foaming, a temperature below the boiling point of the alkaline solution is preferably maintained at all times.

Aqueous mercaptide solutions subjected to our process may contain organic substances such as alcohols, alcohol ethers, alkanolamines, etc. which may have been added to the alkaline reacting hydroxides to act as solutizers for mercaptans in the aqueous hydroxides to aid in the extraction. Such organic substances do not interfere with our process, provided they are less readily oxidized than mercaptides. The presence of salts of aromatic hydroxy compounds of the type of phenol, cresols, xylenols, however, interfers with the oxidation of mercaptides insofar as these substances are oxidized jointly with the mercaptides to undesirable compounds which frequently are of a tarry character. Carboxylic acids such as fatty acids or naphthenic acids or their salts may be oxidized to hydrocarbons and carbon dioxide, the latter being converted to carbonate which cannot be easily reconverted to the hydroxide. Hydrogen sulfide salts are oxidized to thiosulfates and other oxy-sulfur compounds which use an equivalent amount of caustic.

Since hydrogen sulfide, carboxylic acids and hydroxy aromatic compounds frequently are constituents of petroleum oils, we usually pretreat such oils in a manner to remove them prior to extracting the mercaptans. Such pretreatment may be accomplished, for instance, by fractionally distilling the petroleum oil to eliminate hydrogen sulfide, water washing to remove the low fatty acids, treating with a concentrated aqueous alkali soap solution containing free alkali to extract hydroxy aromatic compounds, or treating with a weak aqueous alkali solution to wash out naphthenic acids and/or hydrogen sulfide. In general, hydroxy aromatic compounds are less readily eliminated by pretreatments than carboxylic acids and/or hydrogen sulfide, and therefore the former are most likely to contaminate the alkaline solutions of mercaptides. We have found that as long as the molal ratio of hydroxy aromatic compounds to mercaptides in the solution does not exceed about 1, sufficiently high current efficiencies can be maintained, particularly in the presence of catalysts of a type hereinafter described, to make the process commercially practical.

During the electrolytic treatment of the mercaptide solution, negatively charged mercaptide ions travel to the anode where they are discharged according to the equation:

$$2RS^- \rightarrow RSSR + 2E^-$$

Where RS^-=mercaptide ion

E^-=negative electric charge

Instead of forming disulfides on the anode, the mercaptides may also be converted to sulfonic acids. Whereas, disulfides are neutral compounds which are insoluble in aqueous alkaline reacting hydroxides and are easily separated therefrom by settling, centrifuging or washing with a suitable solvent such as naphtha, sulfonic acids form water soluble sulfonates with many of the aforementioned alkaline reacting hydroxides, and cannot be separated from aqueous alkaline solutions by simple means. If sulfonic acids are produced, the alkaline reacting hydroxide is gradually converted to sulfonates, which are not readily reconverted to the hydroxides. Therefore, it is our aim to maintain such conditions as to avoid the oxidation of mercaptides to sulfonates as much as possible.

It appears that the oxidation of mercaptides to sulfonates depends upon the discharge of hydroxyl ions on the anode, so that anything that will prevent the discharge of hydroxyl ions will also prevent the formation of sulfonates. Hydroxyl ions have a higher discharge voltage than mercaptides, and, therefore, it has been found desirable to operate in the narrow voltage range, in which mercaptide ions, but not hydroxyl ions are discharged. The minimum voltage at which mercaptide ions are discharged at a practical rate is about 1.5 volts. Under many circumstances, however, the voltage drop across the cell may rise considerably above this minimum, thus promoting the discharge of hydroxyl ions; such fluctuations preferably should be avoided. The main factors controlling this over-voltage are anodic current density, concentration and type of mercaptides, catalysts, nature of anode, temperature of treatment and alternating electric potentials superimposed on the direct current.

The higher the anodic current density, i. e. the amperes per unit area of the anode, the higher is also the over-voltage. This places a definite limit on the current density, which we found must not exceed about 10 amperes per square decimeter even under the most favorable conditions. Under less favorable conditions, a lower density must be maintained. The maximum permissible density must be established experimentally for each set of conditions by sampling the aqueous alkaline reacting hydroxide after passage through the cell and determining analytically the amount of sulfonic acids contained therein. If a substantial amount of sulfonates is found in the outgoing solution, the current density must be reduced.

In order to maintain a relatively high current at a minimum current density, it is desirable to enlarge the surface of the anode as

much as possible, for instance by corrugating the rotor in Figure 1.

The maximum permissible amount of sulfonate in the hydroxide is entirely a question of economical considerations, and cannot be specified with any degree of accuracy. It appears, however, that if about 10% or more of the mercaptides are converted per pass to sulfonic acids, the hydroxide will soon be rendered resistant to practical regeneration.

The effect of the current density on the formation of sulfonates is well illustrated by the following figures in which .1 normal solution of butyl mercaptan in a 4 normal sodium hydroxide solution was electrolyzed:

Current density amp./sq. decimeter	Sulfonic acid in percent of total mercaptide oxidized
	Percent
1.16	1.2
1.75	12.5

We found that the resistance toward conversion to sulfonates varies considerably with different mercaptides. As a general rule, tertiary mercaptides are more easily converted to sulfonates than secondary or primary mercaptides, and the resistance increases with increasing length of the carbon chain.

The concentration of mercaptides is of importance, since for a given current density, the over-voltage increases with decreasing concentration. Hence at low concentrations of mercaptides, there is a relatively greater danger of forming sulfonates, and currents of relatively low current densities must be used. Since it is desirable to use high current densities wherever possible to reduce the time of oxidation and the size of treating equipment to a minimum, we may begin treating a mercaptide solution with a current of relatively high density. As the mercaptide concentration decreases, due to the conversion of mercaptides to disulfides, we then reduce the current density just enough to avoid substantial formation of sulfonates. This method of treating may be carried out in a single cell by gradually increasing the resistance in the electric circuit by means of an adjustable rheostat; or in a series of cells of the type shown in the aforedescribed Figure 2, a current density being maintained in each cell which is lower than that of the preceding cell, the difference being sufficient to counteract the effect of decreasing mercaptide concentration on the formation of sulfonates.

In order to avoid local depletion of mercaptides from the immediate vicinity of the anode, which may lead to the liberation of free oxygen, we usually keep the solution in a state of high turbulence. This has the additional advantage of immediately removing disulfides formed in the process from the anode, thereby reducing the danger of rendering a portion of the anode inactive due to accumulation of disulfides thereon.

A number of anions capable of forming water soluble salts with the aqueous hydroxide were found to be active as catalysts in the matter of lowering the over-voltage required to discharge mercaptide ions. Anions of acids containing elements of the third group of the periodic system, sixth group in the 4 and 6 valent state and seventh group in the 1 and 5 valent state are suitable for this purpose. Particularly useful are the following: borate, sulfite, sulfate, selenite, selenate, tellurite, tellurate, chromate, fluoride, chlorate, bromide, bromate, iodine and iodate ions.

While the effective concentration of these catalyst ions may vary over a considerable range, an average of about .005 mol per liter was found practical in most instances.

Certain of these catalysts, such as the chromate and selenite ions catalyze the discharge of mercaptides in preference to that of other oxidizable compounds that may be contained in the aqueous alkaline reacting hydroxide, for instance, compounds of the type of cresols. Thus if it should be desired to convert mercaptides to disulfides in spite of the presence of oxidizable impurities other than mercaptides which tend to interfere with our process, this can be done successfully by adding one or several of the above catalysts to the mercaptide solution.

The following data illustrate the effect of a typical catalyst on the formation of sulfonates: A .1 normal solution of ethyl mercaptide in a 4 normal sodium hydroxide solution was oxidized with and without borate as catalyst with the following results:

Sulfonates in per cent of total mercaptide oxidized

Current density amp./sq. decimeter	Catalyst	
	None	.005 mol $BO_3^{\equiv}$ per liter
.58	4.8	2.5
1.75	22.3	11.5

In some instances the nature of the anode appears to have an effect on the formation of sulfonates. In particular, smooth platinum metals appear to be conducive to this reaction, while other suitable electrode materials are more or less inactive.

With increasing temperature of the treatment, the formation of sulfonates appears to be slightly reduced. This result seems to be mainly due to a rather pronounced decrease of the over-voltage required to discharge mercaptide ions with increasing temperature.

A low amperage alternating current of not more than 100 cycles having a density lower than that of the direct current, superimposed on the direct current also greatly lessens the over-voltage. For instance, when a 60 cycle alternating current of .2 ampere was added to a direct current of 4.0 amperes passing through a mercaptide solution, the amount of oxygen formed was reduced to about one-half.

We claim as our invention:

1. In a regenerative process of extracting mercaptans from sour hydrocarbon oils containing same with an aqueous alkali hydroxide solution capable of extracting mercaptans, thereby forming water-soluble mercaptides, the improvement comprising treating a sour hydrocarbon oil with said hydroxide solution, whereby a spent alkaline solution of mercaptides is formed, separating the treated hydrocarbon oil from the spent solution, passing a direct electric current of sufficient voltage between electrodes through the solution to oxidize mercaptide ions to water-insoluble disulfides, while maintaining an anodic current density below 10 amps./dm.^{2} and below that at which a substantial portion of the mercaptides is converted to sulfonates, and separating the disulfides from the electrolyzed aqueous solution.

2. The process of claim 1 in which the aqueous

solution contains an effective quantity of a catalyst anion capable of reducing over-voltage required to discharge mercaptide ions, said catalyst anion being selected from the group of borate, sulfite, sulfate, selenite, selenate, tellurite, tellurate, chromate, fluoride, chlorate, bromide, bromate, iodide, and iodate ions.

3. The process of claim 1 in which an alternating current of less than 100 cycles having a density below that of the direct current is superimposed on the direct current.

4. The process of claim 1 in which the aqueous solution is kept in a turbulent state to prevent local depletion of mercaptide ions from the immediate vicinity of the anode.

5. In a regenerative process of extracting mercaptans from sour hydrocarbon oils containing same with an aqueous alkali hydroxide solution capable of extracting mercaptans, thereby forming water-soluble mercaptides, the improvement comprising treating a sour hydrocarbon oil with said hydroxide solution, whereby a spent alkaline solution of mercaptides is formed, separating the treated hydrocarbon oil from the spent solution, and flowing the latter through at least two separate serially arranged electrolyzing zones, passing through the solution contained in each zone direct electric current of sufficient voltage to oxidize mercaptide ions to water-insoluble disulfides, while maintaining in the several zones progressively decreasing anodic current densities in the direction of the flow of the solution, said current densities being lower than those at which a substantial portion of the mercaptides are oxidized to sulfonates and below 10 amps./dm.^{2}, and separating the disulfides from the electrolyzed aqueous solution.

6. The process of claim 5 in which the disulfides are separated from the solution after each passage through an electrolyzing zone.

7. In a continuous regenerative process of extracting mercaptans from sour hydrocarbon oils containing same with an aqueous alkali hydroxide solution capable of extracting mercaptans, thereby forming water soluble mercaptides, the improvement comprising treating a sour hydrocarbon oil with said hydroxide solution, whereby a spent alkaline solution containing mercaptides is formed, separating the treated hydrocarbon oil from the spent solution, passing a direct electric current of sufficient voltage between electrodes through the latter to oxidize mercaptide ions to water insoluble disulfides while maintaining an anodic current density below 10 amps./dm^2, regulating same with decreasing content of mercaptides to keep it below that at which a substantial portion of the mercaptides is converted to sulfonates, separating the disulfides from the electrolyzed aqueous solution and returning the latter for further extracting mercaptans from sour hydrocarbon oil.

8. In a continuous regenerative process of extracting mercaptans from a sour hydrocarbon oil containing same and acidic compounds other than mercaptans, with an alkali hydroxide solution capable of extracting mercaptans, thereby forming water soluble mercaptides, the step of pretreating the sour hydrocarbon oil to remove the acidic compounds without effecting sweetening, treating the pretreated oil with said hydroxide solution, whereby a spent alkaline solution containing mercaptides is formed, separating the treated hydrocarbon oil from the spent solution, passing a direct electric current of sufficient voltage between electrodes through the latter to oxidize mercaptide ions to water insoluble disulfides while maintaining an anodic current density below 10 amps./dm.^{2}, regulating same with decreasing content of mercaptides to keep it below that at which a substantial portion of the mercaptides is converted to sulfonates, separating the disulfides from the electrolyzed aqueous solution and returning the latter for further extracting mercaptans from pretreated sour hydrocarbon oils free from acids other than mercaptans.

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