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PROCESS FOR TREATING HYDROCARBONS

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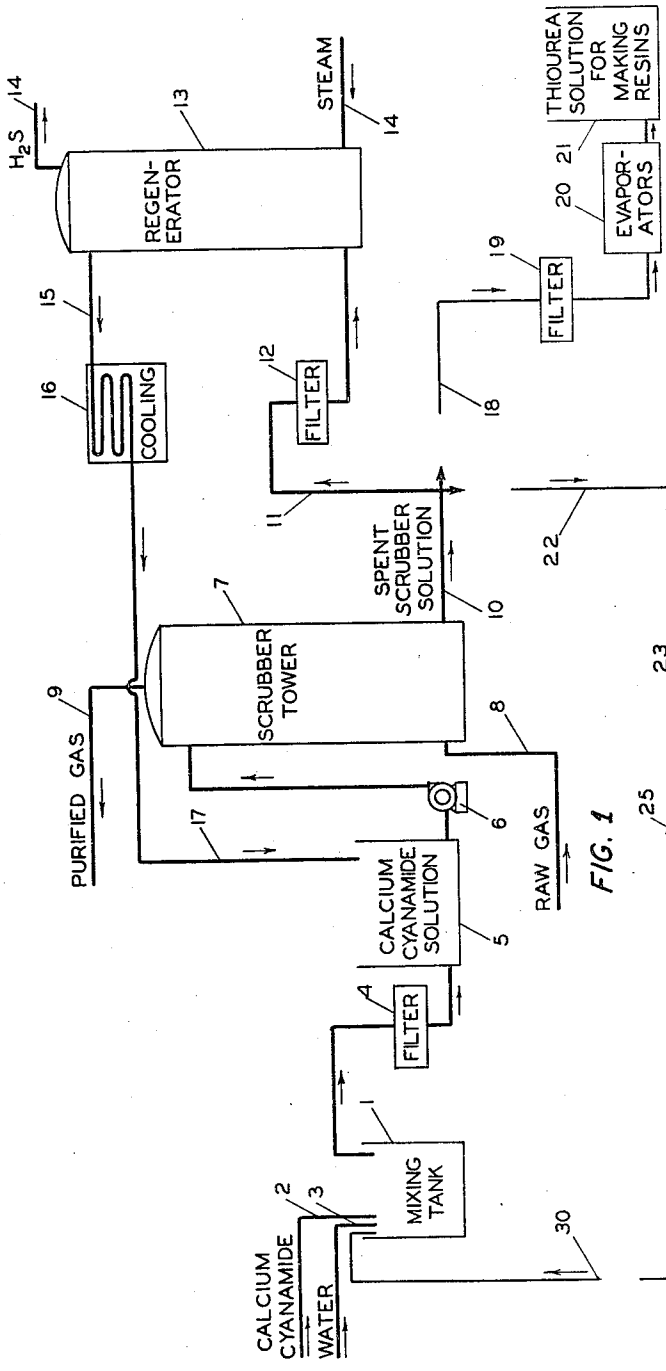


FIG. 1

FIG. 2

FIG. 3

INVENTOR.
W. B. LERCH
C. H. MATHIS
E. J. GATCHELL

BY Hudson, Young, Linkley & Yingst
ATTORNEYS.

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PROCESS FOR TREATING HYDROCARBONS

William Bruce Lerch, Clyde H. Mathis, and Eugene J. Gatchell, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

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8 Claims. (Cl. 196—30)

This invention relates to the use of cyanamide compounds for the removal of hydrogen sulfide and for other objectionable sulphur compounds, mercaptans, etc. from gaseous or liquid hydrocarbons. The invention further relates to the process of using the hydrogen sulfide and objectionable sulphur compounds present in the gaseous or liquid hydrocarbons to react with a cyanamide compound to form thiourea and isothiourea ethers.

Gaseous or liquid hydrocarbons, particularly crude gasoline contain appreciable quantities of sulphur compounds, as mercaptans, and it is the usual practice to remove them or convert them to harmless compounds by an appropriate chemical treatment. This process is referred to among oil technologists as "sweetening." A sweetened gasoline is sweet to the doctor test. That is, it shows no discolorization when treated with alkaline sodium plumbite and sulphur.

The improved method of refining petroleum hydrocarbon products herein set forth is of special value and application in the treatment of light petroleum distillate such as natural gasoline, refinery straight run and cracked gasolines, kerosenes, petroleum solvent naphthas, liquefied petroleum gases, and the like. Such unrefined petroleum products contain mercaptans which give the products undesirable odors and render them corrosive and unstable. Petroleum hydrocarbon products containing mercaptans are commonly termed "sour." Conversion of these mercaptans partially or entirely to disulfides, or completely removing them, is usually termed "sweetening." Customarily, these "sour" compounds are altered, or removed by chemical treatment of the "sour" hydrocarbon fluid with alkali plumbite and sulphur. In some instances, particularly with natural gasoline sweetening is accomplished with alkaline hypochlorite solution but like the alkali plumbite method, this method has proved to be not only uneconomical and cumbersome but also has been found to introduce undesirable constituents into the products being sweetened, such constituents in many instances of high mercaptan content products being as detrimental to the petroleum products treated as those present originally. Still other methods have been suggested for the removal or conversion of mercaptans but in nearly every instance these methods involve numerous treating steps, requiring close control, so that the increase in operating costs renders them uneconomical.

An object of the present invention is to provide a process by which the sour compounds in sour oils, distillates or gas may be removed or altered, or converted into compounds which are not sour, thus rendering the sour oils, distillates or gases sweet, and in which process, if desired, the agent or agents employed to sweeten the sour oils, distillates or gases may be reactivated or regenerated concurrently with their use in the sweetening of the sour oils, distillates or gases, whereby the sweetening of the sour oils, distillates or gases and the maintenance of the activity of said agent or agents may be effected at the same time.

A further object of the invention is the provision of a process by which sour oils, distillates, or gases, may be sweetened without the use of the so-called doctor solution, that is an aqueous solution of sodium plumbite and also without the use of aqueous solutions of salts of metals forming insoluble sulfides with hydrogen sulfide, such as aqueous solutions of cupric chloride or other cupric salts.

A still further object of the invention is to provide a process in which, if desired, the spent agent or agents employed to sweeten the sour oils, distillates or gases may be processed to secure a thiourea solution instead of reactivating the same for use in sweetening the sour oil, distillate or gases.

A still further object of the invention is to provide a process in which, if desired, the spent agent or agents employed to sweeten the sour oils, distillates or gases may be acidified and then processed to secure thiourea crystals.

Other objects and advantages along with the foregoing will be apparent to those skilled in the art to which the present invention pertains from the disclosure thereof hereinafter set forth, and are attained by the invention described in detail below.

In the accompanying drawing we have shown diagrammatically certain kinds of apparatus which may be used in carrying out the treatment, but it is to be understood that the invention is in no sense restricted to these particular types of apparatus.

Figure 1 shows a diagrammatic view of one modification of the process wherein the sweetening process has regenerative apparatus for the spent agent or agents,

Figure 2 shows a diagrammatic view of another modification of the process wherein the sweetening process is connected with apparatus to process the spent agent or agents so as to recover a thiourea solution,

Figure 3 shows a diagrammatic view of another modification of the process wherein the sweetening process is connected with apparatus to process the spent agent or agents with an acid so as to recover thiourea crystals and a filtrate.

Calcium cyanamide or any cyanamide compound will remove mercaptans from hydrocarbons as well as removing the hydrogen sulfide. The cyanamide and mercaptan react to form isothiourea ethers which are quite insoluble in the solvents present.

Referring more particularly to Figure 1, which constitutes a proposed showing of apparatus for the preferred modification of the process for the removal of hydrogen sulfide from gases by the use of commercial calcium cyanamide, 1 represents a mixing tank wherein calcium cyanamide from line 2 is mixed or dissolved in water from line 3. It is essential that the temperature in the mixing tank be kept below 25° C. throughout the mixing. From the mixing tank 1, the suspension passes through the filter 4 where it is filtered and the filtrate containing the calcium cyanamide is fed continuously into the top of the scrubber tower 7 from storage tank 5 by means of pump 6. It is to be noted that sulphur, thiourea, ammonia or other amines may be added as a catalyst to the calcium cyanamide solution when the same is in the storage tank 5. The raw gas, enters the scrubber tower 7 at the bottom thereof through the line 8 and the purified product leaves at the top through line 9. The raw gas, in passing up through the scrubber tower 7, is continuously being subjected to the calcium cyanamide solution, and the hydrogen sulfide reacts with the calcium cyanamide solution to change the composition of the same and allow a purified product to leave the scrubber tower through the line 9. The spent scrubber solution leaves the bottom of the tower 7 through the line 10. This spent scrubber solution contains thiourea, calcium sulfhydrate and a precipitate of calcium carbonate formed from the calcium cyanamide and carbon dioxide contained in most natural gas.

The spent scrubber solution can be treated by three different methods after it leaves the tower and the first to be discussed will be that portion on the right of Figure 1. The spent scrubber solution passes from the line 10 to the line 11 into filter 12 from where it is pumped into regenerator 13. Steam is entering the bottom of regenerator 13 through the line 14 and supplies heat to the solution in regenerator 13. In the regenerator 13, the calcium sulfhydrate is broken down into calcium hydroxide and hydrogen sulfide by heating. When the thiourea is heated in the presence of catalysts such as mercuric chloride, lead peroxide, mercuric oxide or lead hydroxide, it loses hydrogen sulfide and yields cyanamide. Sufficient catalyst is present at all times in the regenerator 13 to allow these reactions to proceed to completion. Cyanamide and calcium hydroxide react to form calcium cyanamide and water, the starting substance, which leaves the regenerator at the top thereof by line 15, passes through cooler 16 and is placed in the storage tank 5 through line 17 to be recirculated through the scrubber tank 7. The hydrogen sulfide gas leaves the top of the regenerator tank 13 through the line 14 and may be disposed of in any way desirable. By this method it is necessary to add only enough calcium cyanamide to compensate for mechanical losses. The theoretical reaction involved in this process is illustrated in the following chemical equations:

$$\underset{\text{Calcium sulfhydrate}}{Ca(SH)_2} + \text{heat (steam)} = \underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Hydrogen sulfide}}{2H_2S}$$

$$\underset{\text{Thiourea}}{CS(NH_2)_2} + \text{heat (steam)} + \text{catalyst} = \underset{\text{Hydrogen sulfide}}{H_2S} + \underset{\text{Cyanamide}}{CN{\cdot}NH_2}$$

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Cyanamide}}{CN{\cdot}NH_2} = \underset{\text{Water}}{2H_2O} + \underset{\text{Calcium cyanamide}}{CaCN_2}$$

Referring now to Figure 2 which shows a modification of the previously described apparatus, the spent scrubber solution may now be taken through line 18 with line 11 completely closed, or the solution may be divided in any proportions desired and passed through both lines 11 and 18. The spent scrubber solution passing through line 18 passes to filter 19 where the solution is filtered and thence to evaporator 20 where some of the liquid is evaporated off. The steps under this process are carried out preferably under reduced pressure and the evaporation proceeds until the thiourea reaches concentration suitable for use in making synthetic resins and is stored in tank 21. If the line 11 is completely closed, by this method there is no recycling of the spent material, instead it is used as a raw material for the manufacture of resins or other purposes for which it is applicable.

Referring to the process shown in Figure 3, the spent scrubber solution may pass from line 10 to line 22 or the solution may be divided in any proportions desired between the other two lines, and passed to the mixer tank 23. Connecting into tank 23 is the line 24 which delivers a dilute sulphuric acid or any other acid to the tank and mixes the same with the spent scrubber solution to acidify the same and the whole is cooled. If desired, in place of the dilute sulphuric acid, the carbon dioxide from the flue gases may be used where such is available. Hydrogen sulfide is driven off from the spent scrubber solution and the residue goes to the filter 26. The filtrate is evaporated in evaporator 27 from where the fluid passes to crystallizing tank 28. The solution then passes to filter 29 where the thiourea crystals are removed from the filter and the filtrate is pumped back to mixing tank 1 through pipe 30 where it dissolves more crude calcium cyanamide or if desired may be discarded.

This process of removing hydrogen sulfide is continuous by any of the methods described. It may be a method of removing hydrogen sulfide in which only enough fresh chemical for makeup is required, or it may be a method of removing hydrogen sulfide from gas which yields a source of thiourea for industrial purposes. It is to be understood that while sour gas has been used to illustrate the apparatus shown in the drawing, similar setups could be used for sweetening other sour hydrocarbons and it is not to be understood that the process is limited only to gas.

It is not essential to have a complete plant as just described but a suspension of calcium cyanamide in a tower equipped with proper agitation affords an efficient method of hydrogen sulfide removal, however, the recovery of thiourea is more difficult. Calcium cyanamide, for instance, may be used dry, as a paste, or a suspension in a solvent such as water to remove hydrogen sulfide from hydrocarbons such as natural gas, coal gas, producer gas, water gas, refinery still gas, or liquid hydrocarbons such as crude oil or the fractions obtained therefrom or any gases or liquid materials containing hydrogen sulfide.

We prefer to use calcium cyanamide because of its availability and low cost but do not limit ourselves to this compound since cyanamide, sodium cyanamide or other cyanamide salts may be used equally as well and are to be considered within the scope of this invention. In practice the gas or hydrocarbon vapor, for instance natural gas, containing hydrogen sulfide is conducted through a bed of dry calcium cyanamide or is scrubbed with a solution or suspension of calcium cyanamide in water or other solvent in the conventional countercurrent type of scrubber. The theoretical reaction involved is illustrated in the following chemical equation:

$$\underset{\text{Calcium cyanamide}}{CaCN_2} + \underset{\text{Hydrogen sulfide}}{3H_2S} = \underset{\text{Calcium sulfhydrate}}{Ca(SH)_2} + \underset{\text{Thiourea}}{CS(NH_2)_2}$$

According to this equation, one weight equivalent, for instance 80 pounds, of calcium cyanamide should react with three weight equivalents or 102 pounds of hydrogen sulfide to form as one of the products of the reaction one weight equivalent or 76 pounds of thiourea which may be separated as a valuable by-product. In practice it has been found that a much greater weight of hydrogen sulfide is required to react with the same weight of calcium cyanamide which would indicate that the reaction is more complex than that indicated by the chemical equation as given.

This process has several advantages over the well-known method of circulation of a solution of caustic soda or sodium hydroxide for the removal of hydrogen sulfide. The calcium cyanamide is cheaper than caustic soda and pound for pound it has a much greater capacity for absorbing hydrogen sulfide. Thus theoretically one pound of caustic soda will unite with 0.85 pound of hydrogen sulfide according to the equation:

$$\underset{\text{Sodium hydroxide}}{NaOH} + \underset{\text{Hydrogen sulfide}}{H_2S} = \underset{\text{Sodium sulfide}}{Na_2S} + \underset{\text{Water}}{H_2O}$$

In practice it has been found that one pound of commercial calcium cyanamide will unite with 2.3 pounds of hydrogen sulfide.

If desired, it is not necessary to have the calcium cyanamide in solution with water but the same may be used in a dry state. Dry granular calcium cyanamide may be packed in an upright cylindrical tank which should be equipped with coils cooled by circulating water to maintain the temperature below 100° F. and the gas containing hydrogen sulfide is passed upwardly through the tank. The gas contacts the calcium cyanamide and the hydrogen sulfide is absorbed rapidly with the process continuing until the effluent gas shows traces of hydrogen sulfide when the flow of gas is switched to another similar absorber while the spent calcium cyanamide in the first cylinder is extracted with solvents to remove the thiourea after which the absorber is cleaned and recharged with a fresh batch of calcium cyanamide and is ready for a new cycle of operation. In treating gasoline or kerosene to remove the sulphur compounds, this treatment may be applied by passing the vapors over a bed of calcium cyanamide or cyanamide.

From the foregoing it is believed that the steps and advantages of the process may be readily understood by those skilled in the art and it is manifest that changes may be made in the details disclosed without departing from the spirit of the invention, as expressed in the claims. In the appended claims, we mean the term "hydrocarbons" to generically define gasoline, kerosene, and other petroleum distillates and oils.

Having thus described our invention, what we claim is:

1. The process of removing sulphur compounds from hydrocarbons which comprises passing said hydrocarbons through a bed of dry cyanamide.

2. The process of removing sulphur compounds from hydrocarbons which comprises passing said hydrocarbons through an aqueous cyanamide solution.

3. The process of removing sulphur compounds from hydrocarbons which comprises passing said hydrocarbons through a bed of dry cyanamide compound.

4. The process of removing sulphur compounds from hydrocarbons which comprises passing said hydrocarbons through an aqueous cyanamide compound solution.

5. The process of removing sulphur compounds from hydrocarbons which comprises passing said hydrocarbons through a bed of dry calcium cyanamide.

6. The process of removing sulphur compounds from hydrocarbons which comprises passing said hydrocarbons through an aqueous calcium cyanamide solution.

7. The process of sweetening hydrocarbons which comprises treating said hydrocarbons with calcium cyanamide in a scrubber tower, conducting the spent scrubber solution to a regenerator to reconvert the spent solution to calcium cyanamide and then recirculating the regenerated calcium cyanamide solution through the scrubber tower.

8. The process of sweetening hydrocarbons which comprises treating said hydrocarbons with calcium cyanamide in a scrubber tower conducting the spent scrubber solution to a regenerator where it is reconverted to calcium cyanamide solution in the presence of a catalyst and steam and then recirculating the regenerated calcium cyanamide solution through the scrubber tower.

WILLIAM BRUCE LERCH.
CLYDE H. MATHIS.
EUGENE J. GATCHELL.