

## Description

This invention relates to a method for the removal of  $H_2S$  and/or ash from molten sulfur. More specifically this invention relates to the removal of residual  $H_2S$  and/or ash or ash forming compounds from molten sulfur by the addition to the molten sulfur of one or more compounds described hereinafter which promote the removal of  $H_2S$  and hasten the decomposition of hydrogen polysulfides to  $H_2S$ , and/or which promote the flotation and agglomeration of ash and/or ash forming compounds to the surface of the molten sulfur where it can be removed.

In many petroleum processing operations in which hydrogen sulfide is present in a gas stream, particularly in treating tail gas from the reaction of  $H_2S$  and  $SO_2$  to produce elemental sulfur, the remaining hydrogen sulfide is removed by passing the gas stream through a venturi/absorber section where the hydrogen sulfide is absorbed by an aqueous solution containing salts. The hydrogen sulfide is converted to elemental sulfur which is subsequently precipitated from the scrubbing solution for further treatment. This sulfur, which may contain from about 30 to more than 12,000 parts per million by weight (wppm) of salt impurities, may be sent to a separate sulfur retention facility or it may be blended with relatively large quantities of low ash sulfur. In either event it is desirable to reduce the concentration of ash-forming compounds in the sulfur, since these compounds may adversely affect subsequent processing of the sulfur. For example in the production of sulfuric acid from sulfur, the sulfur is first burned to  $SO_2$  in a spray jet burner. Salts and other impurities in the sulfur may form ash that plugs the orifices of the burner nozzles. As used hereinafter the term "ash-forming compounds" is defined to mean any impurity in the molten sulfur which forms an ash-type residue when burned or strongly heated. Generally, the ash-forming compounds in the sulfur will be primarily inorganic salts from the absorption process which inadvertently become entrained in the sulfur, although other ash-forming compounds also may be present.

Another concern in the manufacture of elemental sulfur is the presence of  $H_2S$  and compounds that decompose to  $H_2S$  in the sulfur.

During the manufacture of elemental sulfur, particularly by the reaction of:



small quantities of  $H_2S$  and hydrogen polysulfides, typically 150—300 parts per million by weight (wppm), may remain in the molten sulfur. During storage the hydrogen polysulfides decompose to hydrogen sulfide, which is slowly released by the sulfur. This slow release of hydrogen sulfide is undesirable for several reasons. Since the threshold odor limit of  $H_2S$  in air is relatively low, approximately 0.1 parts per million by volume (vppm), this slow release may create nuisance odors. Moreover,  $H_2S$  is highly toxic, flammable and may form explosive mixtures with air. Accordingly, the presence of  $H_2S$  in molten sulfur is being limited in many locations by increasingly stringent regulations.

Several methods have been used to decrease the residual hydrogen sulfide and hydrogen polysulfides concentration in sulfur. One method has been merely to allow a "weathering off" process to take place before the sulfur is transported. But, this is a relatively slow process that requires large sulfur storage capacity.

A method for increasing the rate of this "weathering off" process uses a circulatory spraying system. However, this requires the purchase and use of additional circulatory equipment and may not reduce the residual hydrogen sulfide and hydrogen polysulfide to sufficiently low levels.

Other methods have involved the addition of chemical compounds and sulfur dioxide to the molten sulfur to convert the hydrogen sulfide and hydrogen polysulfides to elemental sulfur. British Patent No. 1,393,967 describes a method for reducing the amount of hydrogen polysulfides and hydrogen sulfide by in situ reaction to form elemental sulfur. Sulfur dioxide and an additive, which is an inorganic alkali metal compound, ammonia, an ammonium compound or a basic organic compound with at least one amino group, is injected into the liquid sulfur while the sulfur is flowing through a conduit. Table I of this patent indicates that large amounts of  $H_2S$  remain in the molten sulfur when  $SO_2$  is not added together with the additives noted. U.S. Patent No. 3,447,903 discloses the addition of certain classes of compounds together with  $SO_2$  to molten sulfur for a variety of purposes, including the removal of small quantities of hydrogen sulfide. Among the classes of compounds disclosed are:

- (a) Ammonia and its organic derivatives having a  $K_b$  greater than  $10^{-10}$ ;
- (b) Primary, secondary and tertiary alkyl, aryl and cyclic amines having a  $K_b$  greater than  $10^{-10}$ ;
- (c) Quaternary basic nitrogen compounds that decompose between  $20^\circ C$  and  $160^\circ C$  to yield ammonia or its inorganic derivatives having a  $K_b$  value greater than  $10^{-10}$ ; and
- (d) Quaternary basic nitrogen compounds that on heating to temperatures between  $20^\circ C$  and  $160^\circ C$ , decompose to yield an organic amine having a  $K_b$  value greater than  $10^{-10}$ . However, this process requires the further addition of sulfur dioxide to react with the  $H_2S$  in place and form sulfur rather than liberating the  $H_2S$ .

Use of  $SO_2$  to remove  $H_2S$  from molten sulfur is not desirable for several reasons. Sulfur dioxide is difficult to store, since it is gaseous at ambient conditions. Thus, means must be provided for injecting the  $SO_2$  directly into the molten sulfur and for adjusting the relative quantities of  $SO_2$  and the other additive metered into the molten sulfur. In addition,  $SO_2$  is toxic, a strong irritant to the eyes and mucous

membranes and an air contaminant. Moreover,  $\text{SO}_2$  is corrosive to the carbon steel surfaces of some sulfur handling facilities. These factors may complicate or restrict its use in commercial facilities.

U.S. Patent No. 3,278,269 describes several classes of compounds which may be added to molten sulfur to improve the friability of solidified sulfur. The compounds disclosed include the following:

5 A. Liquid and solid primary, secondary and tertiary alkyl, aryl, and cyclic amines having a  $K_b$  value greater than  $10^{-10}$  in which the amino nitrogen is attached to a primary, secondary or aromatic hydrocarbon;

B. Quaternary nitrogen compounds that decompose between  $20-160^\circ\text{C}$  to yield ammonia; and

10 C. Quaternary nitrogen compounds that on heating to temperatures between  $20$  and  $160^\circ\text{C}$  decompose to yield an organic amine having a  $K_b$  value greater than  $10^{-10}$  in which the carbon atom directly attached to the amino nitrogen is primary, secondary or aromatic.

U.S. Patent No. 3,364,655 discloses that  $\text{H}_2\text{S}$  can be removed from liquid sulfur by atomizing the sulfur, and that this process can be further improved by the addition of ammonia. No method for removing ash-forming compounds are disclosed.

15 In *Z. Anal. Chem.* 166 (1959) pages 274-283 Schmidt and Talsky describe a method to convert hydrogen polysulfides to hydrogen sulfide by the addition to the sulfur of sulfites or cyanides.

French patent specification No. 2185587 (FR-A-2185587) and corresponding U.K. patent specification No. 1433822 (GB-A-1433822) describes a process for removing hydrogen sulfide from molten sulfur, the hydrogen sulfide being dissolved in the molten sulfur as hydrogen polysulfide, which 20 process comprises adding a nitrogen-containing compound to the molten sulfur and introducing into the molten sulfur an oxidizing gas containing oxygen and/or sulfur dioxide at an elevated pressure and in a finely-divided condition while the molten sulfur is confined en masse in a tank or other containing means. The oxidizing gas may be heated to avoid excessive cooling of the molten sulfur. The said nitrogen-containing compound may be ammonia (or a salt thereof), an amine including alkylamine or 25 hydroxylalkylamine, urea or a substituted urea, and is preferably diethanolamine or di-isopropanolamine.

Some of the drawbacks of using sulfur dioxide in a process to remove hydrogen sulfide from molten sulfur are mentioned above. The use of an oxidizing gas containing oxygen (with or without sulfur dioxide) is subject to the following further drawbacks, namely the risk of increased corrosion rates of the molten sulfur facilities; the increased risk of fire and/or explosion; the use of additional energy to inject the 30 oxidizing gas into the molten sulfur. When the oxidizing gas is heated to avoid excessive cooling of the molten sulfur, still further energy is required. The cost of the energy thus used is a factor in the viability of the process.

It is desirable to provide a process in which the residual hydrogen sulfide and hydrogen polysulfides are reduced to relatively low levels without the use of excessively large, or corrosion resistant storage 35 facilities.

It is also desirable to provide a process in which the hydrogen sulfide and hydrogen polysulfides can be reduced to relatively low levels in the molten sulfur by the addition of agents that do not require complex addition or metering facilities.

It is also desirable to provide a reliable, relatively inexpensive process which may reduce the 40 concentration of ash-forming compounds in the molten sulfur.

It is also advantageous to provide a process in which the hydrogen sulfide and hydrogen polysulfides are reduced to lower levels by the addition of chemical compounds that do not significantly increase the ash content of the product sulfur and may, in certain instances, reduce the product sulfur ash content.

The present invention provides a method for reducing the concentration of hydrogen sulfide and 45 hydrogen polysulfides and/or ash-forming compounds in molten sulfur, comprising the addition to the molten sulfur of an agent selected from inorganic and organo-phosphorus compounds, dithionates, dithionites, thiosulfates, bisulfides, bisulfites, urea and urea derivatives without the addition to the molten sulfur of an oxidising gas such as a gas containing oxygen and/or sulfur dioxide.

Among the preferred inorganic phosphorus compounds are the phosphates, phosphines, phosphites, 50 phosphine oxide, phosphine sulfide and hypophosphates. Among the preferred urea derivatives are mono-, di-, tri- and tetra-ureas, thiourea, and cyclic ureas. In one preferred method an aqueous solution of the agent or a melt of the agent is metered by gravity flow into the molten sulfur. In another method, an aqueous solution or a melt of the agent is pumped into the molten sulfur.

When the agent reduces the ash-forming compounds present in the molten sulfur, at least a portion of 55 the ash-forming compounds rise to, and collect at the surface of, the molten sulfur where they can be removed.

#### Brief description of the drawings

Figure 1 is a plot of the percentage of the hydrogen sulfide and hydrogen polysulfides removed from 60 samples during a 2.5 hour period as a function of the agent concentration for three agents.

Figure 2 is a simplified drawing of a molten sulfur facility with means for adding an agent to the sulfur.

Figure 3 is a plot of the residual  $\text{H}_2\text{S}$  concentration in sulfur as a function of time after starting the addition of a specific agent.

#### Detailed description of the invention

65 Molten sulfur from conventional sulfur recovery sources typically may contain as much as 50-500

parts per million by weight (wppm) of ash and 700 parts per million by weight (wppm) of  $H_2S$  and hydrogen polysulfides. The agents used to convert hydrogen polysulfides to hydrogen sulfide and/or to reduce the concentration of ash-forming compounds preferably should be effective at relatively low concentrations and be relatively easily volatilized from the sulfur so that they do not adversely affect the residual ash content of the product sulfur. The compounds described hereinafter have been found to be effective agents at relatively low concentrations. Many of the compounds described hereinafter are readily volatilizable. This further minimizes their effect on product sulfur ash content. It has been found that certain classes of compounds are effective agents as indicated below:

A. Sulfur compounds comprising dithionates, dithionites, thiosulfates, bisulfides and bisulfites. Among the preferred compounds are easily volatilizable salts, such as ammonium, phosphonium and alkyl ammonium salts. Specific preferred compounds are ammonium thiosulfate and ammonium bisulfite. A non-ammonium salt which is effective is sodium dithionite.

B. Inorganic and organo-phosphorus compounds including phosphates, hypophosphates, phosphines, phosphites, phosphine oxides and phosphine sulfides.

Preferred compounds are the easily volatilized salts, such as ammonium phosphonium and alkyl ammonium salts. Specific preferred compounds are triammonium orthophosphates, diammonium hydrogen phosphate and triphenyl phosphine.

C. Urea and urea derivatives, including but not limited to urea, thiourea, mono-, di-, tri-, and tetraureas and cyclic ureas.

Preferred compounds are those easily volatilized, such as urea and thiourea.

Samples of candidate agents were screened for effectiveness in  $H_2S$  degassing according to the following procedure. Samples of molten sulfur were taken from the combustor rundown line of a commercial sulfur plant so that sulfur having the highest  $H_2S$  levels would be obtained for testing purposes. The samples, approximately 150 ml each, were poured from a sample dipper directly into spoutless 300 ml Berzelius beakers which also were used to contain the sulfur during analysis. The samples were kept hot during transport to the laboratory. A three-hole rubber stopper equipped with a thermometer and two unequal lengths of glass tubing was placed in the beaker opening. One piece of glass tubing extended below the surface of the sulfur while the other terminated above the surface. Each compound screened was added to a stirred sulfur sample maintained at  $130^\circ C$ . Dry nitrogen was sparged through each sample for 2.5 hours with the released  $H_2S$  and exiting nitrogen being directed through two gas absorption bottles containing a 3% zinc acetate solution. After the sulfur was purged for 2.5 hours, the two gas absorption bottles were removed and replaced by two gas absorption bottles containing fresh 3% zinc acetate solution positioned as previously described.

Although lead sulfide is known in the art to be highly effective in promoting the decomposition of hydrogen polysulfides to  $H_2S$ , this compound is not used commercially to degas molten sulfur because of toxicity concerns from the presence of trace amounts of lead in the sulfur and because lead sulfide would increase the ash content of the sulfur. This known effectiveness of lead sulfide was used as a standard to determine the degassing characteristics of the compounds screened. One gram of lead sulfide was then added to the sulfur samples containing the agents to decompose any hydrogen polysulfides which had not been removed by the agent added during the first 2.5 hour period. Dry nitrogen was again sparged through the molten sulfur for a 2.5 hour period, the exiting nitrogen and  $H_2S$  passing into the absorption train. The gas absorption bottles from the first and second 2.5 hour periods were poured into separate beakers for titration by a standard iodometric method. A known quantity of standardized iodine solution was added to each beaker and the unreacted iodine subsequently back-titrated with a standardized thiosulfate solution. This method is described in more detail in the *Analytical Chemistry of Sulfur and Its Compounds*, Edited by J. H. Karchmer, Part I, John Wiley & Sons, NY Pages 63-66 (1970). The effectiveness of each compound screened was determined by comparing the amount of  $H_2S$  removed during the first 2.5 hour period with that removed during the second 2.5 hour period. The higher the ratio of the  $H_2S$  removed during the first period relative to the second period, the more effective was the additive. Analytical results for various compounds tested are shown in Tables I, II and III at additive concentrations of 200, 100 and 50 weight parts per million (wppm) respectively, in the molten sulfur. In Table I, all samples having the same test group number were drawn on the same day and have comparable initial  $H_2S$  values.

0 045 636

TABLE I  
Tests at 200 wppm additive level

| 5  | Test group | Additive                                                      | First 2.5 hr. with additive (ppm H <sub>2</sub> S) | Second 2.5 hr. with PbS (ppm H <sub>2</sub> S) | Total (ppm H <sub>2</sub> S) |
|----|------------|---------------------------------------------------------------|----------------------------------------------------|------------------------------------------------|------------------------------|
|    | 1          | None                                                          | 246                                                | 282                                            | 528                          |
| 10 | 1          | H <sub>2</sub> O (<1000 ppm)                                  | 167                                                | 355                                            | 522                          |
|    | 2          | NH <sub>4</sub> Cl                                            | 218                                                | 272                                            | 490                          |
|    | 2          | NH <sub>4</sub> HSO <sub>4</sub>                              | 259                                                | 266                                            | 525                          |
| 15 | 3          | (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> | 314                                                | 310                                            | 624                          |
|    | 3          | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 619                                                | 3                                              | 622                          |
| 20 | 3          | Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>                 | 583                                                | 6                                              | 589                          |
|    | 3          | (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P               | 625                                                | 32                                             | 657*                         |
|    | 4          | NH <sub>4</sub> SCN                                           | 331                                                | 190                                            | 521                          |
| 25 | 4          | (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>               | 497                                                | 4                                              | 503                          |
|    | 5          | CO(NH <sub>2</sub> ) <sub>2</sub>                             | 486                                                | 18                                             | 504                          |
| 30 | 6          | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> | 213                                                | 159                                            | 372                          |
|    | 7          | (NH <sub>2</sub> ) <sub>2</sub> CS                            | 614                                                | 0                                              | 614                          |
| 35 | 8          | NH <sub>4</sub> CO <sub>2</sub> H                             | 335                                                | 498                                            | 833                          |

\* Some phosphine carried by the sparge gas into the solution causes an artificially large value because the analysis cannot distinguish between phosphines and H<sub>2</sub>S.

TABLE II  
Tests at 100 wppm additive level

| 40 | Additive                                                      | First 2.5 hrs. with additive | Second 2.5 hr. with PbS | Total H <sub>2</sub> S (wppm) |
|----|---------------------------------------------------------------|------------------------------|-------------------------|-------------------------------|
| 45 | NH <sub>4</sub> HSO <sub>3</sub>                              | 289                          | 153                     | 442                           |
|    | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub>               | 421                          | 25                      | 446                           |
|    | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 428                          | 2                       | 430                           |
| 50 | (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>               | 374                          | 93                      | 467                           |

TABLE III  
Tests at 50 wppm additive level

| 55 | Additive                                                      | First 2.5 hrs. with additive | Second 2.5 hr. with PbS | Total H <sub>2</sub> S (wppm) |
|----|---------------------------------------------------------------|------------------------------|-------------------------|-------------------------------|
|    | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub>               | 401                          | 145                     | 546                           |
| 60 | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | 418                          | 162                     | 580                           |
|    | (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>              | 496                          | 74                      | 570                           |
| 65 | (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>               | 272                          | 310                     | 582                           |

The relative degassing ability of the compounds may be seen more clearly by their effectiveness at low concentrations in the sulfur. The relative effectiveness of three selected compounds in degassing sulfur at varying concentrations in the sulfur may be seen from Figure 1, in which the agent concentration is plotted against the percent of the total  $H_2S$  released in the first 2.5 hours.

The data in Table I show that the ammonium ion is not the portion of the ammonium salt that was active in degassing the molten sulfur. For example, ammonium chloride and ammonium bisulfate were totally ineffective as degassing agents. Even ammonium salts of weaker acids such as oxalic, formic and carbonic acids were much less effective than the best degassing agents tested, ammonium thiosulfate, ammonium phosphate, and sodium dithionite. Ammonium compounds may be added to the molten sulfur at temperatures at which substantially no ammonia is produced, since it appears that ammonia is not essential for effective implementation of the method of the present invention.

The ability of certain of the agents to reduce the concentration of ash-forming compounds then was determined as follows. The ash content of the molten sulfur sample with no agent present and with one agent, ammonium thiosulfate, was determined and is presented in Table IV. In both series of tests the ash determination involved merely burning a 100 gram sample of the sulfur in a preweighed crucible and weighing the ash remaining in the crucible after combustion and subsequent cooling in a desiccator.

The ability of ammonium thiosulfate to reduce the ash contents of samples both high and low in inorganic salt levels was determined in the presence of concrete and carbon steel.

Samples of sulfur were kept at 130—140°C for 24 hours while suspended within them were small blocks of concrete and small samples of carbon steel. Two thousand wppm of ammonium thiosulfate was added to one sample while another was left with no agent. Both the treated sulfur and the untreated control were sampled from their top strata and from near the bottom of their respective containers. These tests were done with samples both low and high in ash content. The results are shown in Table IV.

TABLE IV  
Ash tests in presence of concrete and carbon steel

|                    | Treated sample<br>(2,000 ppm $(NH_4)_2S_2O_3$ )<br>ash content (wppm) | Untreated sample<br>(no additive)<br>ash content (wppm) |
|--------------------|-----------------------------------------------------------------------|---------------------------------------------------------|
| Low ash sulfur     |                                                                       |                                                         |
| Sample from top    | 8.7                                                                   | 2.9                                                     |
| Sample from bottom | 25.6                                                                  | —                                                       |
| High ash sulfur    |                                                                       |                                                         |
| Sample from top    | 269                                                                   | 139                                                     |
| Sample from bottom | 10,280                                                                | 11,780                                                  |

The ammonium thiosulfate caused no corrosion of metal or damage to concrete in these tests. The rate of corrosion of carbon steel actually decreased after the addition of ammonium thiosulfate.

It should be noted that the ash content of the treated samples is higher than the controls for the samples taken from the top. The effectiveness of the ammonium thiosulfate in causing ash forming compounds to float to the top may be seen from the sample having the high salt content. The sample from the top of the treated sample was higher in ash content than the control, while the sample from the bottom of the treated sample was lower in ash content than the control.

In laboratory tests it was found advantageous to have continuous stirring of the sulfur during the degassing process. In two hour tests, substantially similar to those previously described, a significantly greater amount of  $H_2S$  was degassed when the sample was stirred, than when no stirring was done, as shown in Table V.

TABLE V  
 $H_2S$  Removal wppm from samples

| No stirring | Continuous stirring |
|-------------|---------------------|
| 265 and 296 | 408                 |

Based upon these tests it was believed that continuous mixing was necessary for reducing the concentration of ash-forming compounds and the hydrogen sulfide and hydrogen polysulfide concentrations to relatively low levels in commercial facilities. Surprisingly, however, in a commercial-sized installation the sulfur could be degassed to relatively low levels merely by gravity feeding the agent into the molten sulfur through the inspection box or look box in the inlet line to the sulfur pit.

After addition of the agent was started, the residual concentration of hydrogen sulfide and hydrogen polysulfides decreased with time to relatively low levels. Such an agent addition system has several advantages over complex mixing, metering and/or recirculation systems. The simplicity of this system greatly decreases equipment purchase and operating costs, while providing a more reliable, trouble-free addition system.

In Figure 2 a preferred embodiment for adding the agent to a conventional molten sulfur facility is shown. The facility comprises an inlet, inspection box, outlet and sulfur pit. In this figure, many lines, valves and all instrumentation have been omitted for simplicity. Molten sulfur leaving the sulfur recovery system passes through inlet 10 at a temperature in excess of 114°C, typically about 130 to about 165°C. The sulfur then passes through seal 20 and line 30 into inspection box 40. The molten sulfur, typically containing about 50 to about 650 wppm of hydrogen sulfide and hydrogen polysulfides and from about 0 to about 50 wppm of ash-forming compounds leaves inspection box 40 through line 50 for storage and cooling in a sulfur storage facility such as sulfur pit 60. A solution, preferably an aqueous solution, of at least one of the agents is metered into inspection box 40 from storage tank 70 through line 80. Alternatively, if the melting point of the specific agent utilized is below the temperature of the molten sulfur, the agent may be added as a melt. To minimize the equipment required, storage tank 70 may be placed above inspection box 40, and the agent gravity fed. The flow rate is controlled by metering valve 90. The agent solution or melt also may be metered into the molten sulfur installation using a conventional pump. A filter 100 also may be added to minimize contamination of the molten sulfur and to prevent plugging of metering valve 90.

In many locations the tail gas from the reaction of  $H_2S$  and  $SO_2$  for producing elemental sulfur is treated to remove small amounts of  $H_2S$  by a series of reactions in an aqueous solution containing inorganic salts. Occasionally these inorganic salts are carried into the product sulfur. In one test an agent, ammonium thiosulfate, was added as an aqueous solution having 55 wt. % ammonium thiosulfate to molten sulfur having a temperature ranging between about 125 and 150°C. The concentration of ammonium thiosulfate in the sulfur entering the sulfur pit without mechanical agitation was approximately 118 wppm. The average residence time of the sulfur in the pit was 70–80 hrs. It was noted within the first few hours that a thick crust formed on the sulfur surface. As indicated in Table VI the ash content of the sulfur, measured in a sample taken from the pit surface, was 74–85 wppm before the addition of ammonium thiosulfate was started. After 70 hours from the start of the ammonium thiosulfate addition, the ash content of the sulfur dropped to 47–55 wppm but the  $H_2S$  content of the sulfur was not significantly reduced. Later tests with an aqueous solution containing 20–40 wt. % urea showed that it, too, has the property of causing this separation of ash from sulfur and formation of a layer that may be skimmed from the sulfur surface.

To determine if the crust formed on the surface of the sulfur may have inhibited the volatilization of hydrogen sulfide from the sulfur pit, a test using an aqueous solution having 55 wt. % ammonium thiosulfate as the agent was done in a four-stage sulfur pit having a total average residence time of about 6 hours, but with mechanical sulfur recirculation.

TABLE VI  
Effect of adding ammoniumthiosulfate in a conventional sulfur pit on the  $H_2S$  concentration of sulfur

| Time after addition of $(NH_4)_2S_2O_3$ started, hrs. | $H_2S$ Concentration in sulfur; wppm |                | Ash content of sulfur; wppm |                    |
|-------------------------------------------------------|--------------------------------------|----------------|-----------------------------|--------------------|
|                                                       | In sulfur pit                        | Exiting sulfur | Sulfur pit                  | From loading truck |
| 0 (i.e. before addition started)                      | 219, 220, 220, 236                   | —              | 74, 85                      | —                  |
| 20                                                    | 231, 237                             | 190, 194       | —                           | 74, 71             |
| 43                                                    | 241, 176                             | 218, 264       | —                           | 71, 70             |
| 66                                                    | 181, 188                             | —              | —                           | —                  |
| 70                                                    | 199, 114                             | 164, 164       | —                           | 47, 55             |
| 89                                                    | 201, 189, 210                        | —              | —                           | —                  |
| 171                                                   | 213, 224                             | —              | —                           | —                  |

Stages 1, 2 and 3 were equipped with sulfur recirculation pumps having 160, 130 and 150 GPM capacities, respectively, equivalent to 605.7, 492.1 and 567.8 litres/minute respectively, to recirculate the sulfur within the same stage. These results are presented in Table VII and indicate that on a commercial scale ammonium thiosulfate effectively catalyzes the degassing of sulfur.

TABLE VII  
Effect of ammonium thiosulfate on the performance of sulfur  
degasification facility with circulation

| Set of<br>samples No. | Time after<br>addition of<br>(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in the<br>run started, hrs. | Ammonium<br>thiosulfate<br>addition rate,<br>wppm | Residence time<br>of sulfur in<br>each stage, hrs. | 1st stage | 2nd stage | 3rd stage | 4th stage                                               |
|-----------------------|------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|----------------------------------------------------|-----------|-----------|-----------|---------------------------------------------------------|
| 1                     | —                                                                                                                      | 0                                                 | 1.2                                                | 259—263   |           |           | (Inactive without<br>recirculation<br>pumps)<br>185—194 |
| 2                     | —                                                                                                                      | 0                                                 | 1.6                                                | 339       | 228       | 204       | 315                                                     |
| 3                     | —                                                                                                                      | 0                                                 | 1.6                                                | 275       | 211       | 168       | 170                                                     |
| 4                     | 5 1/2                                                                                                                  | 50                                                | 1.4                                                | 76        | 20        | 6         | 5                                                       |

H<sub>2</sub>S Concentration in sulfur, wppm

It should be noted that the hydrogen sulfide and hydrogen polysulfides concentration in Table VII decrease after the addition of ammonium thiosulfate when the sulfur was recirculated. The data of Tables VI and VII thus indicate that ammonium thiosulfate is effective as an ash flotation agent and also as a degassing agent. In a similar test on sulfur having a relatively high ash content of approximately 600 wppm, a crust of inorganic salts formed when aqueous solutions having 20—40 wt. % urea were added to the molten sulfur to a concentration of approximately 40—160 wppm urea, thus indicating that urea is also an effective ash flotation agent. The combination of reducing the concentration of ash forming compounds in the sulfur and degassing the sulfur can be achieved by removing the ash forming compounds from the surface of the sulfur. This may be achieved by conventional liquid-solid separation means. Among the methods which appear to be particularly applicable are skimming the surface of the sulfur pit and passing at least the upper portion of the molten sulfur through a filtration means.

Figure 3 is a plot of the residual  $H_2S$  concentration in molten sulfur contained in a non-stirred sulfur pit where the sulfur, to which about 100 wppm of urea was added using an aqueous solution of 40 wt. % urea had an average residence time ranging from about 3.5 to about 6 days. The residual concentration of  $H_2S$  decreased significantly, illustrating that continuous use of urea also decreases the residual  $H_2S$  concentration of the sulfur even in the absence of sulfur agitation. The ash content of the sulfur, both at the commencement and termination of the test, remained at less than 5 wppm, thus indicating that the urea addition did not adversely affect the ash content of the sulfur.

The concentration of agent utilized is not critical and will be dependent on the specific agent used. Generally, the rate of addition of the agent to the molten sulfur will range between 1 (one) part per billion and 5000 parts per million by weight, and preferably from about 50 to about 200 parts per million by weight.

The equilibrium constant  $K_s$  is described in the book "The Chemistry of Organic Compounds" by J. B. Conan and A. H. Lott, published by Macmillan, 3rd Edition, 1947 (N.Y.) at page 187 et seq.

In Tables V and VI, the multiple readings for each data point result from the fact that each sulfur sample was unmixed and separate portions of the unmixed samples were subjected to laboratory examination and analysis.

### 30 Claims

1. A method for reducing the concentration of hydrogen sulfide and hydrogen polysulfides and/or ash-forming compounds in molten sulfur comprising the addition to the molten sulfur of an agent selected from inorganic and organo-phosphorus compounds, dithionates, dithionites, thiosulfates, bisulfides, bisulfites, urea and urea derivatives without the addition to the molten sulfur of an oxidizing gas such as a gas containing oxygen and/or sulfur dioxide.

2. The method of claim 1 characterized by the inorganic and organo-phosphorus compounds being selected from phosphates, phosphines, phosphites, phosphine oxides, phosphine sulfides and hypophosphates.

3. The method of claim 1 or claim 2 characterized by the inorganic phosphorus compounds being selected from triammonium ortho-phosphate and diammonium hydrogen phosphate.

4. The method of any one of claims 1 to 3 characterized by the urea derivatives being selected from mono-, di-, tri- and tetra ureas, thiourea and cyclic ureas.

5. The method of any one of claims 1 to 4 characterized in that the said agent is selected from ammonium thiosulfate, ammonium dithionate, ammonium dithionite and sodium dithionite.

6. The method of any one of claims 1 to 5 characterized by the rate of addition of the agent to the molten sulfur ranging from about 1 part per billion ( $10^9$ ) to about 5000 parts per million by weight.

7. The method of any one of claims 1 to 6 characterized by the rate of addition of the agent to the molten sulfur ranging from about 50 to 200 parts per million by weight.

8. The method of any one of claims 1 to 7 characterized by the agent added being urea.

9. The method of any one of claims 1 to 8 characterized by the removal of the ash-forming compounds from the molten sulfur.

10. The method of any one of claims 1 to 9 characterized by the removal of  $H_2S$  from the molten sulfur.

### 55 Patentansprüche

1. Verfahren zur Verringerung der Konzentration von Schwefelwasserstoff und Polyschwefelwasserstoffen und/oder aschebildenden Verbindungen in geschmolzenem Schwefel, gekennzeichnet durch die Zugabe eines Mittels ausgewählt aus anorganischen und organischen Phosphorverbindungen, Dithionaten, Dithioniten, Thiosulfaten, Bisulfiden, Bisulfiten, Harnstoff und Harnstoffderivaten zum geschmolzenen Schwefel ohne die Zugabe eines oxydierenden Gases wie eines Sauerstoff und/oder Schwefeldioxid enthaltenden Gases zum geschmolzenen Schwefel.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die anorganischen und organischen Phosphorverbindungen ausgewählt sind aus Phosphaten, Phosphinen, Phosphiten, Phosphinoxiden, Phosphinsulfiden und Hypophosphaten.

It should be noted that the hydrogen sulfide and hydrogen polysulfides concentration in Table VII decrease after the addition of ammonium thiosulfate when the sulfur was recirculated. The data of Tables VI and VII thus indicate that ammonium thiosulfate is effective as an ash flotation agent and also as a degassing agent. In a similar test on sulfur having a relatively high ash content of approximately 600 wppm, a crust of inorganic salts formed when aqueous solutions having 20—40 wt. % urea were added to the molten sulfur to a concentration of approximately 40—160 wppm urea, thus indicating that urea is also an effective ash flotation agent. The combination of reducing the concentration of ash forming compounds in the sulfur and degassing the sulfur can be achieved by removing the ash forming compounds from the surface of the sulfur. This may be achieved by conventional liquid-solid separation means. Among the methods which appear to be particularly applicable are skimming the surface of the sulfur pit and passing at least the upper portion of the molten sulfur through a filtration means.

Figure 3 is a plot of the residual  $H_2S$  concentration in molten sulfur contained in a non-stirred sulfur pit where the sulfur, to which about 100 wppm of urea was added using an aqueous solution of 40 wt. % urea had an average residence time ranging from about 3.5 to about 6 days. The residual concentration of  $H_2S$  decreased significantly, illustrating that continuous use of urea also decreases the residual  $H_2S$  concentration of the sulfur even in the absence of sulfur agitation. The ash content of the sulfur, both at the commencement and termination of the test, remained at less than 5 wppm, thus indicating that the urea addition did not adversely affect the ash content of the sulfur.

The concentration of agent utilized is not critical and will be dependent on the specific agent used. Generally, the rate of addition of the agent to the molten sulfur will range between 1 (one) part per billion and 5000 parts per million by weight, and preferably from about 50 to about 200 parts per million by weight.

The equilibrium constant  $K_a$  is described in the book "The Chemistry of Organic Compounds" by J. B. Conan and A. H. Lott, published by Macmillan, 3rd Edition, 1947 (N.Y.) at page 187 et seq.

In Tables V and VI, the multiple readings for each data point result from the fact that each sulfur sample was unmixed and separate portions of the unmixed samples were subjected to laboratory examination and analysis.

### 30 Claims

1. A method for reducing the concentration of hydrogen sulfide and hydrogen polysulfides and/or ash-forming compounds in molten sulfur comprising the addition to the molten sulfur of an agent selected from inorganic and organo-phosphorus compounds, dithionates, dithionites, thiosulfates, bisulfides, bisulfites, urea and urea derivatives without the addition to the molten sulfur of an oxidizing gas such as a gas containing oxygen and/or sulfur dioxide.

2. The method of claim 1 characterized by the inorganic and organo-phosphorus compounds being selected from phosphates, phosphines, phosphites, phosphine oxides, phosphine sulfides and hypophosphates.

3. The method of claim 1 or claim 2 characterized by the inorganic phosphorus compounds being selected from triammonium ortho-phosphate and diammonium hydrogen phosphate.

4. The method of any one of claims 1 to 3 characterized by the urea derivatives being selected from mono-, di-, tri- and tetra ureas, thiourea and cyclic ureas.

5. The method of any one of claims 1 to 4 characterized in that the said agent is selected from ammonium thiosulfate, ammonium dithionate, ammonium dithionite and sodium dithionite.

6. The method of any one of claims 1 to 5 characterized by the rate of addition of the agent to the molten sulfur ranging from about 1 part per billion ( $10^9$ ) to about 5000 parts per million by weight.

7. The method of any one of claims 1 to 6 characterized by the rate of addition of the agent to the molten sulfur ranging from about 50 to 200 parts per million by weight.

8. The method of any one of claims 1 to 7 characterized by the agent added being urea.

9. The method of any one of claims 1 to 8 characterized by the removal of the ash-forming compounds from the molten sulfur.

10. The method of any one of claims 1 to 9 characterized by the removal of  $H_2S$  from the molten sulfur.

### 55 Patentansprüche

1. Verfahren zur Verringerung der Konzentration von Schwefelwasserstoff und Polyschwefelwasserstoffen und/oder aschebildenden Verbindungen in geschmolzenem Schwefel, gekennzeichnet durch die Zugabe eines Mittels ausgewählt aus anorganischen und organischen Phosphorverbindungen, Dithionaten, Dithioniten, Thiosulfaten, Bisulfiden, Bisulfiten, Harnstoff und Harnstoffderivaten zum geschmolzenen Schwefel ohne die Zugabe eines oxydierenden Gases wie eines Sauerstoff und/oder Schwefeldioxid enthaltenden Gases zum geschmolzenen Schwefel.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die anorganischen und organischen Phosphorverbindungen ausgewählt sind aus Phosphaten, Phosphinen, Phosphiten, Phosphinoxiden, Phosphinsulfiden und Hypophosphaten.





3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die anorganischen Phosphorverbindungen ausgewählt sind aus Triammonium-ortho-phosphat und Diammoniumhydrogenphosphat.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Harnstoffderivate ausgewählt sind aus Mono-, Di-, Tri- und Tetraharstoffen, Thioharnstoff und cyclischen Harnstoffen.
5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Mittel ausgewählt ist aus Ammoniumthiosulfat, Ammoniumdithionat, Ammoniumdithionit und Natriumdithionit.
6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Zugaberate des Mittels zum geschmolzenen Schwefel im Bereich von etwa 1 Gew. ppb ( $10^9$ ) bis etwa 5000 Gew. ppm liegt.
7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß die Zugaberate des Mittels zum geschmolzenen Schwefel im Bereich von etwa 50 bis 200 Gew. ppm liegt.
8. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß das zugesetzte Mittel Harnstoff ist.
9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die aschebildenden Verbindungen aus dem geschmolzenen Schwefel entfernt werden.
10. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß  $H_2S$  aus dem geschmolzenen Schwefel entfernt wird.

### Revendications

1. Un procédé pour réduire la concentration du sulfure d'hydrogène et des polysulfures d'hydrogène et/ou des composés formant des cendres dans le soufre fondu, comprenant l'addition, au soufre fondu, d'un agent choisi parmi les composés organiques et inorganiques du phosphore, les dithionates, les dithionites, les thiosulfates, les bisulfures, les bisulfites, l'urée et les dérivés de l'urée, sans addition, au soufre fondu, d'un gaz oxydant tel qu'un gaz contenant de l'oxygène et/ou de l'anhydride sulfureux.
2. Le procédé de la revendication 1, caractérisé en ce que les composés inorganiques et organiques du phosphore sont choisis parmi les phosphates, phosphines, phosphites, oxydes de phosphine, sulfures de phosphine et hypophosphates.
3. Le procédé de la revendication 1 ou de la revendication 2, caractérisé en ce que les composés inorganiques du phosphore sont choisis entre l'orthophosphate triammonique et l'hydrogénophosphate diammonique.
4. Le procédé de l'une quelconque des revendications 1 à 3, caractérisé en ce que les dérivés de l'urée sont choisis parmi les mono-, di-, tri- et tétraurées, la thiourée et les urées cycliques.
5. Le procédé de l'une quelconque des revendications 1 à 4, caractérisé en ce que ledit agent est choisi parmi le thiosulfate d'ammonium, le dithionate d'ammonium, le dithionite d'ammonium et le dithionite de sodium.
6. Le procédé de l'une quelconque des revendications 1 à 5, caractérisé en ce que le taux d'addition de l'agent au soufre fondu est compris entre environ 1 partie par milliard ( $10^9$ ) et environ 5000 parties par million en poids.
7. Le procédé de l'une quelconque des revendications 1 à 6, caractérisé en ce que le taux d'addition de l'agent au soufre fondu est compris entre environ 50 et 200 parties par million en poids.
8. Le procédé de l'une quelconque des revendications 1 à 7, caractérisé en ce que l'agent ajouté est l'urée.
9. Le procédé de l'une quelconque des revendications 1 à 8, caractérisé par l'élimination, du soufre fondu, des composés formant de cendres.
10. Le procédé de l'une quelconque des revendications 1 à 9, caractérisé par l'élimination, du soufre fondu, du  $H_2S$ .