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PROCESS FOR HEAT-TREATING LIQUID SULFUR CONTAINING CARBONACEOUS IMPURITIES

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This invention relates to a process and apparatus for purifying sulfur. More particularly it relates to a process and apparatus for heat treating sulfur to convert dissolved carbonaceous impurities to insoluble carbon-sulfur compounds, hydrogen sulfide, and carbon disulfide.

Sulfur, as used in the trade, is an exceptionally pure material compared with most other common materials. The crude sulfur of commerce is normally required to contain less than 0.5% total impurities.

The most prevalent and troublesome contaminant of sulfur mined by the Frasch process is dissolved carbonaceous matter. It may occur in concentrations as high as 2%, but as little as 0.05% can degrade the normally bright yellow color to a dirty gray; will cause heat-transfer surfaces in molten sulfur tanks to gradually become coated with a carbonaceous scale that interferes with heat transfer; and makes burning of the sulfur difficult by plugging burner nozzles, or covering burning-sulfur surfaces, with a carbonaceous scale. For these reasons, high carbonaceous content reduces the marketability of sulfur, and users frequently demand that sulfur supplied to them be low in carbonaceous content.

Frasch process sulfur producers have attempted to reduce the dissolved carbonaceous matter in their product in a variety of ways, for a number of years.

One of the cheapest and simplest methods that has been used is to spray the liquid sulfur into the air, allowing it to fall in heated collection tanks. This aeration allows some of the more volatile portions of the carbonaceous matter to evaporate into the air. However, it is seldom possible to reduce the carbonaceous content by this method by more than 10%.

A more elaborate variation of this principle that was been used is to flow the liquid sulfur downward over packing in a tower while air is blown upward through it. Only the more volatile portion of the carbonaceous matter is removable by this procedure, and the carbonaceous content is generally reduced by about 15%.

Filtration of the liquid sulfur after agitation with acid, lime, or activated clays has been widely used. This process generally succeeds in reducing the carbonaceous content by about 50%; and it specifically removes most of the coloring portions of the carbonaceous matter, leaving the sulfur bright and clean in appearances, even though it still contains considerable carbonaceous contamination.

Extraction, by contact of the liquified sulfur with a solvent for the carbonaceous matter, e.g., benzene, is another method of purification that has been described (U.S. Patent No. 3,042,503). This method is useful for reducing the carbonaceous matter content from very high initial values, in the range of 1% to 2%, but it is not capable of bringing the content much below 0.2%. Furthermore, the necessary equipment is quite expensive, must be carefully controlled, and involves the hazard of handling a hot, volatile, generally flammable, solvent.

Sublimation, to produce flowers of sulfur, has long been a standard method of purification. This method is quite costly, and the product still contains enough carbonaceous matter to cause it to turn black on boiling.

In 1939, U.S. Patent No. 2,169,261, was granted C. O. Lee on a method and apparatus for distilling sulfur. This process produces a product with no more than 0.01% carbonaceous matter, but the product contains hydrogen sulfide that can be removed only by additional processing. Also, the necessity of blowing down the undistilled residue before the carbon concentration exceeds about 2%, to avoid resulting high viscosity, makes the sulfur loss high if the feed sulfur contains much carbon. The process requires an expensive installation of boilers constructed of specially-chosen corrosion-resistant metals; and corrosion of the boiler parts, regardless of care in choosing special metals, is inevitable, so that periodic replacement of parts is a necessary cost of the operation. In addition, the heat transfer surfaces of the boiler accumulate a scale of carbonaceous material that seriously reduces heat transfer, and results in excessive heating, and corrosion rates, of the heat transfer surfaces.

It has long been known that heating sulfur contaminated with dissolved carbonaceous matter near its boiling point of 832° F. and retaining it at this temperature for 15 to 30 minutes causes some of the sulfur to react with the carbonaceous matter to form hydrogen sulfide, carbon disulfide, and an insoluble carbon-sulfur compound. This reaction was utilized in the aforementioned Lee distillation patent, and was utilized to greater advantage in a process on which Patent No. 2,941,686 was issued in 1960, to V. H. Brogdon et al.

The conversion by heat treatment, of the single-phase system containing sulfur and dissolved, carbonaceous matter, to a three-phase system-containing, sulfur, hydrogen sulfide, carbon disulfide, and insoluble carbonaceous matter, obviously increases the number of possible methods by which a pure sulfur product can be recovered. The Lee patent, supra, distilled the sulfur; the Brogdon et al. patent, supra, distilled the sulfur, but also pointed out that filtration could be used. Settling or centrifugation is also successful if the insoluble carbonaceous matter precipitates in large enough particles.

Of these methods of separating the insoluble carbonaceous matter from the sulfur, only distillation has, in the past, proved to be really practicable. In practice, the insoluble carbonaceous matter precipitates in such a finely-divided state that it will not settle out; centrifuging of a commercially practical nature, is inffective in causing separation; and filtration is excessively expansive because of rapid blinding of the filter medium.

In 1942, R. F. Bacon and R. Fanelli published (Ind. Eng. Chem., 34, pp. 1043–1048) a description of a method of purifying sulfur utilizing the heat-treatment reaction, magnesia being added to scavenge hydrogen sulfide and any acid formed, and to act as a filter aid. They repeated this heat treatment, with magnesia added, about four times, following each heat treatment with a filtration. Their product was of exceedingly high purity, but amounted to only about 20% of the sulfur with which they started, the rest being lost. The process was proposed only for laboratory purposes; and obviously would not be suitable for commercial use in view of the high sulfur loss, the high cost of magnesia in the quantities used, and the probable low filtration rate.

An object of this invention is to provide a commercially practicable method and apparatus for heat treating sulfur contaminated with dissolved carbonaceous matter, that is relatively low in equipment cost, low in operating and maintanance cost, and which has small sulfur losses.

Another object of this invention is to provide a method and apparatus for heat treating sulfur containing carbonaceous material in such a way that most of the carbon-sulfur compound may be removed by filtration with reduced filter blinding and at high filtration rates.

Another object of this invention is to provide a method and apparatus for heat treating sulfur containing carbonaceous material so that the sulfur may be distilled with reduced scaling of heat transfer surfaces.

Another object is to provide a method and apparatus