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PURIFICATION OF CRUDE SULFUR

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This invention relates to the purification of those sulfurs which contain objectionable impurities exemplified by certain crude or Frasch mined sulfurs usually dark in color, from brown to black. More particularly, it may be considered to relate to the production of high grade or substantially pure elemental sulfur from crude and other impure sulfurs containing undesirable amounts impurities.

Very little knowledge as to the constitution of the impurities in such dark or off-color sulfurs is recorded in the literature, these impurities being referred to generally as "carbonaceous" materials. In distillation residues obtained during conventional purification processes, the impurities have been referred to as "tarry" or "bituminous" compounds. It is now considered as a fact that the impurities initially present are hydrocarbons of various undetermined constitutions and that on heating to high temperatures, they react with sulfur forming H_2S and other gaseous sulfur compounds and sulfur-insoluble complex carbon-sulfur compounds, which compounds will sometimes be hereinafter referred to as "carsul."

A number of methods of purifying crude sulfur have heretofore been proposed, but they invariably have either been ineffective in accomplishing adequate purification or they have been wasteful of elemental sulfur or uneconomical for other reasons. For example, crude sulfur distilled in a boiler leaves a viscous waste product composed of elemental sulfur and tarry substances (carsul), such sulfur being present in the waste product in at least a ten-fold quantity in relation to the tarry products, this minimum proportion of sulfur being necessary to provide the fluidity required for removal of the residue from the sulfur boiler. The residual elemental sulfur and the combined sulfur in this waste product has represented a substantial loss. Purification of the dark sulfur by means of filtration with adsorbent clays, has also been proposed, but these treatments following conventional procedures requiring large amounts of clay are only partially effective and furthermore, they are expensive to operate, sulfur being a low price chemical handled in large bulk quantities.

Objects of the present invention are (1) to purify the above described crude or impure sulfurs without any appreciable loss of sulfur either in the form of elemental sulfur or in the form of combined sulfur bound in the impurities originally present or formed during the heating or other purification steps and (2) to accomplish the purification at low cost, both as to the energy consumed and the materials required.

Broadly expressed, the invention may be considered to involve processes for producing or recovering elemental sulfur in pure, or substantial purified form, from crude or impure sulfur (usually containing 0.1 to 3% carbon) which include heating the impure sulfur at a temperature and for a period accomplishing the reaction of the hydrocarbon impurities present with a part of the sulfur so as to form hydrogen sulfide gas which separates out from the reaction mass and to form insoluble carbon-

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sulfur compounds or carsul which remains suspended in the liquefied sulfur mass, next separating the elemental sulfur from the carsul, preferably by distillation, then heating the carsul with or without burning to convert all, or nearly all, of the same into gaseous carbon-sulfur compounds as carbon bisulfide, carbon oxysulfide and/or sulfur dioxide, next mixing the hydrogen sulfide previously produced with any gaseous carbon-sulfur compounds formed and reacting the same, preferably in a Claus kiln, with sulfur dioxide formed by the combustion of at least part of the carbon-sulfur compounds formed, thereby converting the sulfur content of all, or substantially all, of such gases to elemental sulfur.

By the foregoing procedure accomplishing the recovery of both the sulfur separated from the carsul and that produced by the reaction of the sulfur-containing gases, all or practically all of the sulfur present in the crude sulfur is recovered in purified elemental form.

According to one embodiment of the invention hereinbefore broadly described, the carsul separated from the elemental sulfur is burned in a furnace, advantageously in an inclined rotary kiln, with the aid of air introduced into the discharge end thereof, thereby producing sulfur dioxide from the combined sulfur. This sulfur dioxide gas is then mixed with the hydrogen sulfide previously produced and is reacted to produce elemental sulfur as hereinbefore described.

In other important embodiments of the invention, the carsul separated from the elemental sulfur is first heated without burning, by means of combustion gases to a high temperature which converts most of or at least a major portion of the solid carsul (e.g., up to 80–90%) into gaseous carbon-sulfur compounds, principally into carbon bisulfide together with some carbon oxysulfide, the latter or sulfur dioxide being produced if any excess or free air is present in the combustion gases employed in heating the sulfur by direct contact. These gaseous carbon-sulfur compounds (or at least part of them) along with any gaseous sulfur compounds formed by reaction of sulfur or sulfur compounds with the hot flue gases are mixed with the hydrogen sulfide produced during the initial heat treatment and then the mixture is reacted with sulfur dioxide by any process yielding elemental sulfur. The sulfur dioxide may be derived wholly or in part by burning a minor portion of the carsul residue (e.g. 10–20%) left from the above mentioned heat treatment, or it may be obtained by burning part of the gaseous carbon-sulfur compounds resulting from such heat treatment or from the burning of elemental sulfur or from other sources. The sulfur dioxide, of course, may be obtained by combining these two procedures, it being desirable from an economic standpoint to correlate the amount of sulfur dioxide produced with the available amount of sulfur-containing gases (H_2S, CS_2 and COS) produced in the process. By operating in this manner, no difficulty is encountered with any excess of any of the sulfur-containing gases and the recovery of elemental sulfur from the crude sulfur is maintained at a maximum.

The purification processes encompassed by the present invention may be readily understood from the accompanying drawings where two exemplary procedures are diagrammatically illustrated.

In connection with Fig. 1, the crude dark Frasch-mined sulfur containing 0.2% to 1.5% carbon in the form of hydrocarbon impurities, is fed into a preheating tower wherein the sulfur cascades downwardly over trays and flows into a heater which serves primarily as a retention tank, the sulfur mass being heated in the tower to a temperature above 650° F. but below the boiling point (832° F. at atmospheric pressure) of the sulfur at the existing pressure. While the sulfur is in the retention tank-heater at a temperature preferably approaching 832° F., the