United States Patent Office

3,042,503

Patented July 3, 1962

3,042,503

PURIFICATION OF SULFUR

William N. Tuller, White Plains, N.Y., and Frank L. Jackson, Weston, Conn., assignors to Freeport Sulphur Company, New York, N.Y., a corporation of Delaware

Filed Oct. 9, 1958, Ser. No. 766,221

5 Claims. (Cl. 23—310)

This invention relates to the purification of sulfur and more particularly to the removal of carbonaceous or hydrocarbon impurities from crude or mined dark sulfur, specially those sulfurs which contain so much impurity that conventional distillation and adsorption clay methods of purification are too costly.

An object of the present invention is to provide a procedure which is economically acceptable for the removal of carbonaceous impurities from dark sulfurs and the provision of sulfurs of a purity satisfactory for most industrial uses, i.e. those containing less than 0.2% carbon.

Broadly described, the invention may be considered to involve a series of continuous operations including melting the crude or dark sulfur, thereafter flowing the melted sulfur in a readily flowable condition through an extraction zone, flowing a hot liquid solvent for the impurities in countercurrent contact with the flowing sulfur to take up the impurities in the sulfur, collecting the thus purified molten sulfur from one end of the extraction zone and collecting the solvent containing the impurities dissolved therein from its other end.

The solvents found to be effective for accomplishing the purification are any of cycloaliphatic hydrocarbon compounds such as cyclohexane, cyclopentane and methyl cyclohexane; aromatic compounds such as benzene, xylene and toluene; and saturated halogenated aliphatic hydrocarbon compounds such as carbon tetrachloride and ethylene dichloride. Of these classes of solvents the cycloaliphatic and aromatic compounds have, in relation to the halogenated compounds, the advantage of being free of any tendency to become acidic in use. For the most part, the operable solvents have low solubility and miscibility in the liquid sulfur. They are quite stable at operating temperatures, for they do not react with the sulfur and are not easily polymerized or decomposed, and they are not excessively corrosive. The atmospheric boiling points of the most effective solvents are below the ordinary operating temperatures at which the extractions are carried out and when such solvents are employed, the extraction zone must be maintained under pressure to retain the solvent in liquid condition. This property permits the solvent to be separated easily from the sulfur by vaporization.

The amount of solvent used in relation to the sulfur treated is not critical. A solvent to sulfur ratio, by volume, per unit of time of .4 has proven satisfactory. Ratios of 1:1 or 2:1, solvent to sulfur, are operable but use of the higher amount of solvent is generally not justified.

The extraction is preferably carried out in a vertical packed tower, the impure sulfur being introduced near the top and the solvent being introduced near the bottom. The purified sulfur containing a minor amount of residual solvent flows from the bottom of the tower and the solvent containing the impurities together with a minor amount of sulfur flows from the top of the tower. The solvent is preferably recovered by evaporation from the raffinate or purified sulfur and from the hydrocarbon-solvent-sulfur mixture flowing from the top of the tower. The hydrocarbon-sulfur mixture after removal of the solvent from the hydrocarbon-solvent-sulfur mixture can be treated to separate completely the hydrocarbon impurities, but it is economically preferable to effect only a partial purification of the sulfur contained therein and to recycle the same to the extraction tower.

By the steps described above for the treatment of the effluent liquids from the tower, all of the sulfur is purified without loss and the solvent is substantially completely recovered.

In a special embodiment of the invention, the recovery of the solvent from the solvent-hydrocarbon-sulfur mixture leaving the tower is accomplished in two or more evaporators. It has been discovered that although it is relatively easy, using a single evaporator, to separate the solvent from the mixture, it is rather difficult and time consuming to separate the sulfur from the hydrocarbons after the solvent has been separated from the mixture. The high viscosity of the hydrocarbon-sulfur mixture greatly impedes the settling of the sulfur and makes separation of one from the other difficult. It has been found that a multiplicity of evaporators arranged in series can effect a more complete separation of the sulfur from the hydrocarbons in a shorter period of time than can be separated by a single unit. Furthermore the sulfur is obtained in purer form.

As the solvent from the solvent-hydrocarbon-sulfur mixture in the first stage evaporator is vaporized, the concentrations of sulfur and hydrocarbons in the mixture increase and a portion of the dissolved sulfur is precipitated and settled therefrom, suitably from 40 to 80%. Since the hydrocarbons in said mixture are substantially more soluble in the solvent than in the sulfur and since the quantity of solvent in the initial extract is greatly in excess of the quantity necessary to dissolve the hydrocarbons, there is sufficient unvaporized solvent remaining to carry the hydrocarbons to the second stage evaporator. Due to the presence of the solvent in the second stage evaporator, the sulfur settles rapidly from the mixture and can be removed from this stage in a relatively pure state. When several evaporators are employed, portions of dissolved sulfur are recovered from each succeeding unit and sulfur-hydrocarbon-solvent mixtures of decreasing solvent and sulfur content are passed through the units in series. This method of operation separates substantially all of the dissolved sulfur in a relatively short period.

The process of the present invention is particularly applicable to the purification of crude or dark sulfurs which contain not more than about 2% carbonaceous impurities. Substantial amounts of dark sulfur requiring purification for certain uses are now obtained by the conventional mining process based on the Frasch process.

In effecting the extraction process of the present invention, the impure sulfur is melted and treated at a temperature which provides a viscosity below about 95 Saybolt seconds. This degree of fluidity can generally be obtained by maintaining the sulfur during the treatment in the tower at a temperature of from about 217° to 320° F. Surprisingly, the extraction of the impurities from the low viscosity sulfur can be carried out in contact periods measured in seconds or at most in a few minutes. Hence with good contact between the impure sulfur and the solvent, the tower may be relatively short and still accomplish the required degree of purification.

A preferred embodiment of an apparatus for carrying out the process of the invention is illustrated in the diagrammatic drawing.

In connection with the illustrated apparatus, the process of the invention is carried out in the following manner.

Liquid sulfur ordinarily containing about 0.5 to 1.0 percent carbonaceous impurities is pumped from a steam-jacketed feed tank **10** by the force of a pump **11** through a conduit **12** to the top of a packed extraction tower **13**. A solvent of the character hereinbefore defined, suitably amounting to about 40% of the weight of the sulfur when