June 16, 1959 J. W. BARTLETT ET AL 2,890,941

SULFUR EXTRACTION PROCESS

Filed Nov. 18, 1953 2 Sheets-Sheet 1

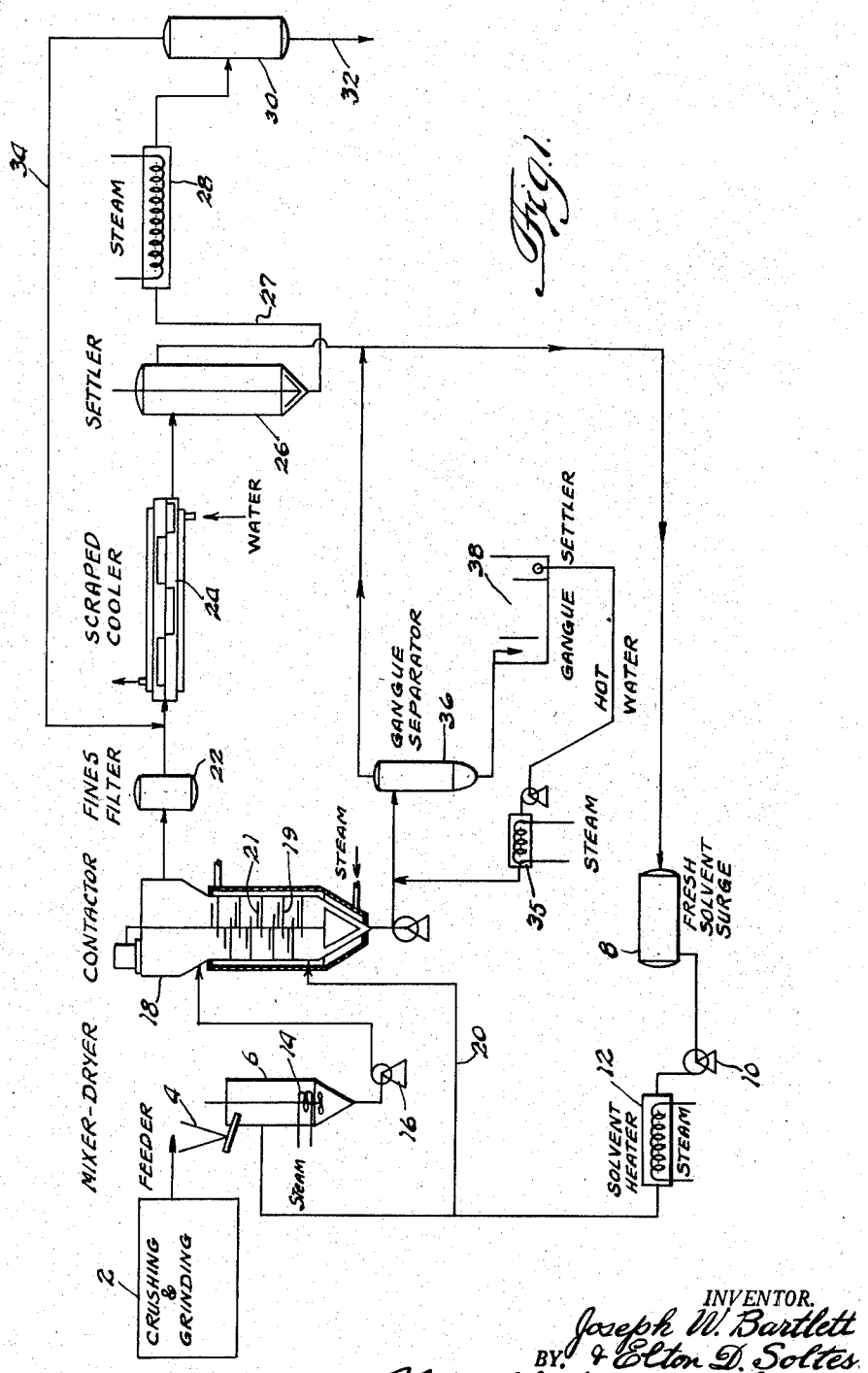



Fig. 1.

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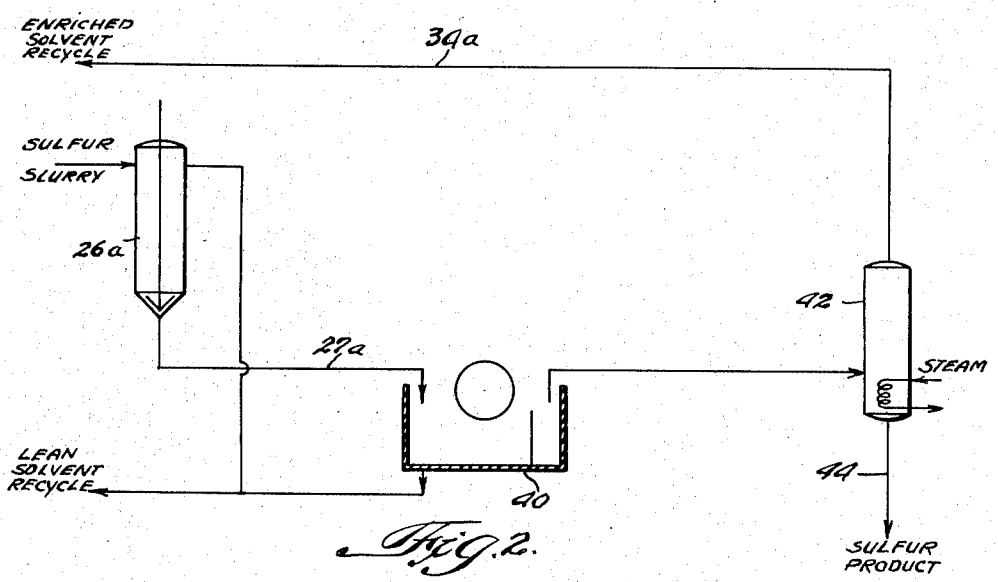



Fig. 2.

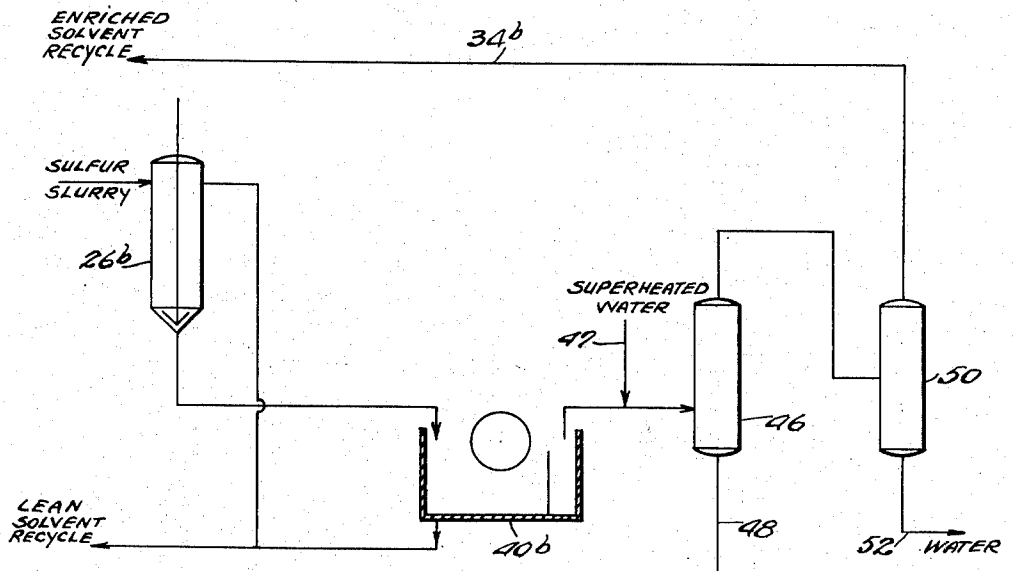



Fig. 3.

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2,890,941

# SULFUR EXTRACTION PROCESS

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Application November 18, 1953, Serial No. 392,840

2 Claims. (Cl. 23—310)

This invention relates to a process of extracting elemental sulfur and has for an object the provision of a process for recovering elemental sulfur from ore or other material containing the same.

A further object of this invention is the provision of a process by which substantially all of the elemental sulfur may be separated from a solid material containing the same.

A still further object of this invention is the provision of a commercially feasible continuous process for extracting elemental sulfur from an ore.

A still further object of this invention is the provision of a process by which substantially pure sulfur may be separated from a sulfur-bearing ore.

A still further object of this invention is the provision of a process which results in the production of sulfur that is essentially free of arsenic and other impurities commonly found in many types of sulfur ores.

An additional object of this invention is the provision of a sulfur extraction process including a preliminary drying step and a step of recovering for recycle the solvent associated with the extracted residue or gangue resulting from the process.

Further and additional objects will appear from the following description, the accompanying drawing and the appended claims.

In accordance with one embodiment of this invention, a continuous process has been devised for extracting elemental sulfur from a sulfur-bearing material by the utilization of a solvent for the sulfur in countercurrent solvent extraction equipment. The sulfur-bearing ore is comminuted and mixed with a first quantity of the solvent to form a slurry which is agitated and maintained at a temperature somewhat in excess of the boiling point of water whereby any moisture normally present in the ore is removed by vaporization and a substantial amount of the sulfur in the ore is dissolved. Thereafter the slurry is passed to a contactor through which the ore particles are passed in countercurrent flow relationship with a second quantity of the solvent. A slurry comprising solvent and gangue essentially free of sulfur is discharged from the contactor. This gangue slurry is then treated with hot water in order to displace the solvent which may be recycled to the system. The temperature within the contactor is preferably maintained in the range between the melting point of sulfur and the higher initial boiling point of the solvent employed. A sulfur-enriched solvent is withdrawn from the top of the contactor essentially free of undissolved solid particles and then cooled, preferably to a temperature lower than about 110° F. in order to precipitate the sulfur. The resulting sulfur-containing slurry is passed to a settler and the bulk of the solvent now lean in sulfur is recycled to the system and the sulfur is recovered as desired. For example, the sulfur precipitate containing some remaining portion of the solvent is heated to a temperature above the melting point of the sulfur and passed to a



decanter in which the melted sulfur settles to the bottom and the top solvent layer is recycled. The molten sulfur may be withdrawn from the decanter and cast into blocks or collected and flaked on a water-cooled flaking drum as desired.

For a more complete understanding of this invention, reference will now be made to the drawings in which:

Fig. 1 is a schematic flow sheet illustrating one embodiment of the process of this invention;

Fig. 2 shows a modification of the final sulfur recovery section; and

Fig. 3 shows another modification of the final sulfur recovery section.

With reference to Fig. 1, a sulfur-bearing ore, suitably one containing from 30 to 40 percent of free sulfur is crushed and ground in suitable grinding equipment 2 and is continuously fed by means of a feeder 4 to a heated mixing and drying chamber 6. At the same time a sulfur solvent which may comprise a hydrocarbon oil having an initial boiling point above about 300° F. is continuously passed from a surge tank 8 through a pump 10 and a heater 12 to the mixer-dryer 6. A solvent that has been found to be particularly suitable for the process of this invention comprises a diesel grade fuel oil having a gravity of 39.3° API and a boiling range between 400° and 600° F. The solvent is heated to between about 250° and 260° F. in the heater 12 and this temperature is maintained in the mixer-dryer 6 by means of a steam-heated coil 14. The amount of ore and solvent added to the mixer-dryer is sufficient to form a flowable slurry which may be continuously pumped by a pump 16 to the upper section of a steam-jacketed contactor 18. The contactor is steam-jacketed to make up for any heat losses to the atmosphere that may occur. The residence time of the slurry in the mixer-dryer 6 is sufficient to dissolve most or all of the sulfur present in the ore and to remove by vaporization substantially all of the free moisture from the ore fed to the process. The latter is desirable since the presence of moisture causes separation difficulties in later stages of the process.

The essentially dry hot slurry is continuously discharged into the upper section of the contactor 18 which latter is provided with a plurality of mechanically scraped trays 19 of conventional design having motor-operated scraper arms 21 which cause the slurry particles to fall from tray to tray as will be understood. At the same time a second quantity of solvent for the sulfur is introduced into a lower section of the contactor 18 by means of conduit 20. The temperature within the contactor 18 is also maintained at between about 250° and 260° F. and it will be understood that the particles of ore pass continuously downwardly over the trays in the contactor 18. At the same time hot solvent passes upwardly in direct countercurrent contact with the solid particles whereby substantially all of the free sulfur is separated therefrom. The sulfur-enriched solvent while still hot is withdrawn from an upper section of the contactor 18 and passed without substantial cooling through a fines filter 22 and then to a water-cooled scraped cooler 24 in which the temperature of the solvent is reduced to less than about 110° F. and preferably between about 70° and 95° F. Because of this temperature drop the sulfur precipitates from the solvent and the resulting sulfur slurry is passed to a settler 26. Cold solvent lean in sulfur is cycled from the upper section of the settler 26 to the fresh solvent surge tank 8. For final recovery a heavy slurry of sulfur containing some solvent is discharged from a lower portion of the settler 26 via line 27 through a steam heater 28 in which the slurry is heated to a temperature above the melting point of the sulfur and the resulting mixture is then discharged into a de-

canter or separator **30**. Essentially pure sulfur, being better than 99% pure, settles to the bottom of the separator **30** in the molten state and is withdrawn therefrom for casting into blocks or otherwise through a line **32**. The hot solvent which is enriched in sulfur is withdrawn from the top of the separator **30** through line **34** for recycle to the scraped cooler **24** or elsewhere in the system, as will be understood.

The sulfur-free gangue is discharged from the lower section of the contactor **18** in the form of a solvent slurry. This slurry is mixed with a stream of hot water heated by a heater **35**. The hot water displaces the solvent in the gangue and the mixture is passed into a gangue separator **36**. Thus in the separator **36** an upper lean solvent layer forms which is cycled to the fresh solvent surge tank **8** or it may be passed directly to the suction of feed pump **10** since it retains a considerable amount of available heat. The gangue and water are passed to a gangue settler **38** wherein the gangue separates by gravity for discharge and the water is recycled to the gangue separator after being further heated in the heater **35**, as will be understood.

It will be apparent from the foregoing description that a simple continuous commercially feasible process has been devised for extracting elemental sulfur from sulfur-bearing ores and other materials. It will be appreciated that the foregoing description is more or less specific to one embodiment of this invention and many changes may be made without departing from the spirit and scope of the claims appended hereto. As previously indicated, the sulfur-bearing ore should be crushed and ground to provide a slurry which may be readily flowed through the system in a continuous manner. Generally speaking, it is preferred that the ore be crushed to a size of less than that corresponding to about 8 mesh. The process described above has been used in connection with sulfur ores containing from about 8 to 45 percent of free sulfur. However, the process is commercially feasible for ores containing higher or lower percentages of free sulfur as will be understood.

In the foregoing description a heavy hydrocarbon oil has been specifically mentioned as the solvent for the sulfur. However, by suitable modifications, other solvents may be employed; for example, suitable solvents for sulfur are known to be aniline, carbon tetrachloride, carbon disulfide, trichlorethylene, tetrachlorethylene, m-xylene, beta-naphthol, phenol, pyridine, sulfur monochloride, benzene, toluene, naphthalene, aliphatic hydrocarbons containing three or more carbon atoms, or mixtures of the foregoing. Generally speaking, however, it is preferred to employ a solvent which under the conditions of operation boils at a temperature higher than the melting point of sulfur. Most efficient extraction is obtained if the temperature is above the melting point of sulfur but lower than the initial boiling point of the solvent employed and lower than the temperature at which sulfur may react with the solvent. Suitably the temperature may range between about 240° and 270° F. where a hydrocarbon solvent having an initial boiling point above about 300° F. is employed. Furthermore, in systems in which water is used to purge solvent from the gangue or from the pure sulfur, the solvent should be substantially unreactive with and immiscible in water to prevent substantial solvent losses.

The ratio of solvent to ore in the process may be varied over a wide range and depends upon the sulfur content of the ore and the solubility of the sulfur in the solvent at a given operating temperature. The solubility of sulfur at 250° F. in the diesel grade fuel oil mentioned above approaches 10% by weight maximum. Thus the total amount of oil contacted with the ore will be (1) sufficient to effect a free-flowing slurry in the mixer-dryer **6**; (2) sufficient added at the bottom of the contactor **18** to insure complete dissolution of the sulfur which in this instance would be a minimum of 10 parts of total oil for each part of available sulfur, preferably in the ratio of about 15 to 1; and (3) sufficient, in addition, to allow for a free-flowing gangue slurry to be discharged from the contactor to permit ready gangue washing. Thus the minimum oil-ore ratio will depend essentially upon how close to saturation it is convenient to operate the process. In an illustrative example, a 30% sulfur ore is fed to the mixer-dryer at the rate of five pounds per minute while a first quantity of the hot solvent above specified is charged to the mixer-dryer **6** at the rate of 2.5 gallons per minute and a second quantity of hot solvent is charged to the lower section of the contactor **18** at the rate of 1.7 gallons per minute. The discharge from the bottom of the contactor **18** is at the rate per minute of 3.5 pounds of gangue suspended in 0.6 gallon of lean solvent. The temperature in the gangue separator **36** is below the boiling point of the water under the pressure maintained therein and is preferably above about 170° F. It is preferred, in accordance with one embodiment of this invention, to operate the gangue separator above 170° F. in order to limit emulsion formation and to permit ready separation of solvent from the gangue.

In precipitating the sulfur from the hot sulfur-enriched solvent, the scraped cooler may be cooled to any temperature which will permit of effective and economical separation of the sulfur. Generally speaking, the enriched solvent should be cooled to a temperature below about 110° F. in order to obtain economical separation under the conditions mentioned in the foregoing specific example. Suitably these cooling temperatures are between about 70° and 95° F. depending upon the temperature of the available cooling water.

It will be appreciated in the foregoing that various items of equipment have been specifically indicated. However, these may be modified or changed in ways that will be apparent to one skilled in the art. For example, other types of contactors may be employed if desired and under certain conditions it may be preferred to employ a number of contactors operated either in parallel or in series for effecting an efficient extraction of the sulfur from the ore.

In order to operate the process of this invention in accordance with the specific embodiment heretofore presented, and as previously suggested, it is important to employ sufficient solvent in the process to provide freely flowing slurries that may be readily pumped and transferred to the various items of equipment. Also sufficient solvent should be employed to permit the extraction of substantially all of the sulfur from the ore and in addition to provide sufficient to form an essentially sulfur-free slurry of gangue which is discharged from the contacting zone.

The process of this invention is operated at substantially atmospheric pressure throughout. However, it will be apparent that the process may be modified so that certain phases of the process will be carried out under superatmospheric pressure, particularly if low boiling solvents are employed. Higher boiling solvents are usually to be preferred because of cost and safety features.

As previously suggested, other methods may be employed for finally recovering the sulfur from the slurry of sulfur and solvent in the settler **26**. One such alternative is shown in Fig. 2. In that embodiment the sulfur-lean solvent is cycled to the system from the settler **26***a* as mentioned above. The concentrated sulfur slurry is passed via line **27***a* to a vacuum filter **40** and the resulting sulfur containing about 5–10% solvent is passed to a steam coil heated melting zone **42**. Pure molten sulfur is discharged through line **44** and sulfur-enriched solvent is cycled as before through line **34***a* to the scraped cooler or elsewhere in the system. Lean solvent from

the filter 40 is cycled to the fresh solvent surge as before indicated.

Another modification employing a filter is shown in Fig. 3. Here the final recovery is essentially the same as that disclosed in Fig. 2 except that the sulfur separated from the filter 40*b* containing 5–10% solvent is melted by direct contact with superheated water introduced through line 47 in the vessel 46. Pure sulfur is withdrawn through line 48 and a mixture of solvent and water passes overhead to a separator 50. This system is useful primarily where the solvent is almost wholly immiscible with water at the temperatures obtaining in the separator 50. The water is discharged through line 52 and enriched solvent is recycled as before indicated via line 34*b*.

The sulfur produced by the extraction process of this invention is of a high order of purity having a high yellow color being substantially free of arsenic and other impurities normally associated with sulfur-bearing ores which, in prior commercial processes, find their way into the final product.

While particular embodiments of this invention are shown above, it will be understood, of course, that the invention is not to be limited thereto, since many modifications may be made, and it is contemplated, therefore, by the appended claims, to cover any such modifications as fall within the true spirit and scope of this invention.

We claim:

1. A continuous process for extracting elemental sulfur of high purity from an ore containing the same and moisture which comprises mixing particles of said ore with a first quantity of a water-immiscible liquid solvent for said sulfur at a temperature above the boiling point of water and for a time sufficient to remove by vaporization substantially all of the water from the resulting slurry, said solvent having a boiling point above the melting point of sulfur and being added in sufficient quantity to form a flowable slurry with said ore particles, passing the resulting moisture-free slurry into a contact zone at one end, passing a second quantity of said water-immiscible liquid solvent into said contact zone at another end for countercurrent flow direct contact relationship with said



slurry, whereby sulfur values in said slurry particles are dissolved in said liquid solvent, withdrawing a slurry of gangue and solvent depleted in sulfur content from said another end of said contact zone and discharging a sulfur-enriched solvent from said contact zone adjacent said one end, the temperature within said contact zone being maintained above the melting point of sulfur.

2. A continuous process for extracting elemental sulfur of high purity from an ore containing the same and moisture which comprises mixing particles of said ore with a first quantity of a water-immiscible liquid solvent for said sulfur at a temperature above the boiling point of water for a time sufficient to remove by vaporization substantially all of the moisture from the resulting slurry, said solvent having a boiling point above the melting point of sulfur, said solvent being added in sufficient quantity and said ore particles being of such a size so as to form a readily flowable slurry, flowing the resulting substantially moisture-free slurry into a contact zone at one end, flowing a second quantity of water-immiscible liquid solvent into said contact zone at another end for countercurrent flow direct contact relationship with the ore particles in said slurry, the temperature within said contact zone being maintained above the melting point of sulfur, flowably withdrawing a slurry of solvent and gangue depleted in sulfur content from said contact zone another end, discharging a sulfur-enriched solvent from said contact zone adjacent said one end, and cooling the discharged sulfur-enriched solvent to precipitate the sulfur therefrom.

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