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PRODUCING INSOLUBLE SULFUR

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This invention relates to the production of a sulfur having a high insoluble sulfur fraction.

It is known that on cooling sulfur from the neighborhood of 400° C., the so-called insoluble form of sulfur (also termed sulfur mu) will be present in the product which forms. Thus Endres, in Patent No. 1,875,372, states that by heating ordinary soluble sulfur to the boiling point and then quenching the molten mass in cold water, a material is obtained which at first is of an amorphous, gummy nature. This, according to Endres, soon sets into a hard, brittle mass which contains approximately one part of insoluble sulfur (S mu) and two parts of ordinary soluble sulfur. The usual practice is to remove the soluble sulfur with a suitable sulfur solvent, such as carbon bisulfide, leaving substantially pure insoluble sulfur.

Another practice which has been adopted for the preparation of insoluble sulfur is to treat flowers of sulfur having a relatively high insoluble sulfur content with a soluble sulfur solvent, such as carbon bisulfide. This practice makes the resulting product comparatively expensive, for one must first produce the flowers of sulfur and then treat them with the soluble sulfur solvent.

I have found that a sulfur containing a relatively high percentage of insoluble sulfur can be produced by quenching sulfur, either in liquid or in vapor form, in a cold aqueous acidic medium having an oxidation-reduction potential which is maintained within certain desired limits. Quenching of sulfur in the form of vapor rather than in liquid form produces the highest insoluble content. Control of the potential is also more essential when the sulfur is in finely divided form, for the reversion of the sulfur from one form to the other appears to start at the surface of each individual particle. Because it is difficult to obtain a finely divided product upon quenching liquid sulfur, the potential has less effect.

The highest insoluble content has been obtained by quenching sulfur vapor in a cold aqueous acid bath having an oxidation-reduction potential of between about 0.67 to about 0.77 volt; material containing 65% and better of sulfur insoluble in carbon bisulfide has been obtained by using baths in this range. As one goes beyond this range, the insoluble content drops for example, between about 0.60 and 0.67 volt and about 0.77 and 0.83 volt, the insoluble sulfur content is well above 50% but is below the value present when the preferred range is

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employed. When the potential is between about 0.3 and 0.60 volt and 0.83 and about 1.2 volts, the content drops to about 45%. In determining the yield of insoluble sulfur at different potentials, the only factor varied was the bath potential, all others being maintained constant. The above results, therefore, truly represent and illustrate the effect of variation of bath potential upon the yield of insoluble sulfur.

The actual insoluble sulfur content obtained for a bath of a given oxidation-reduction potential will depend partly upon the construction of the equipment employed, and the rapidity of quenching effected in the bath. Exact values, therefore, cannot be given for all possible conditions. However, in the same equipment, everything else being otherwise maintained identical, the insoluble sulfur content can be increased several fold by utilizing a cold acidic bath having an oxidation-reduction potential within the ranges specified, and particularly between 0.6 and 0.83 volt.

The yield of insoluble sulfur is enhanced by maintaining the bath at as low a temperature as is feasible, preferably below 50° C. and between about 5° and 20° C. This can be achieved by circulating the bath through a heat exchanger and returning the cooled bath to the quenching vessel.

The acidic bath can be made up in any suitable manner. For example, a bath having an 0.3 volt oxidation-reduction potential is made up of an 0.1 normal sodium sulfite solution containing 18% HCl; a bath having approximately an 0.6 volt potential is made up of a solution containing slightly less than 5% nitric acid and 0.4% iron in the ferric state; a bath having an 0.83 volt potential is made up of a 5% nitric acid solution containing 2% ferric iron; a bath of 1.2 volts potential is made up of an 0.1 normal potassium permanganate solution containing 5% nitric acid. The potential desired can easily be achieved by those skilled in the art and baths of various compositions can be utilized to provide the same oxidation-reduction potential.

It is desirable to measure the oxidation-reduction potential of the bath and to add to the bath, or to the circulating stream from the bath, sufficient of an oxidizing material to maintain the bath within the oxidation-reduction range. This is essential because the vaporized sulfur introduces small quantities of substances, such as hydrogen sulfide, into the bath which lower the potential relatively rapidly.

For example, utilizing a bath consisting of 18%

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hydrochloric acid and having an initial oxidation-reduction potential of 0.335 volt, the bath potential was found to fall to 0.290 volt during the first minute of sulfur vapor introduction, so that the sulfur contained a negligible quantity of insoluble sulfur. When a like bath was made 0.1 normal with respect to sodium sulfite, the potential remained relatively constant and did not fall off to a value outside of the desired range until after some 18 minutes of continuous use. During this period, the sulfur produced contained better than 40% of insoluble sulfur. By checking the bath potential at regular intervals, one can determine its potential and add additional oxidizing material to maintain the bath potential.

In practice, the stream of sulfur is brought into contact with the bath under such conditions that the sulfur is quickly condensed. The bath temperature should be maintained as low as is economically feasible, preferably below 50° C. and usually below 25° C. The sulfur is recovered from the bath, washed free of any bath liquor retained and dried, after which it can be reduced to any desired particle size. To insure that the insoluble sulfur does not revert to the soluble form and to reduce the rate of reversion, the sulfur is preferably washed with a material containing a halogen, bromine, chlorine or iodine, or a halogen containing material such as sulfur chloride or sulfur bromide. The wash, if an aqueous one, should be acid; carbon bisulfide, benzene, toluene, xylene or a petroleum fraction can be used. The wash liquid should be one containing from 0.25% to about 2% of the stabilizing agent. Or after being dried the sulfur can be treated with a small quantity of the halogen or sulfur-halogen to effect the desired stabilization. Sulfur chloride and sulfur bromide are used broadly as referring to the several compounds of definite or indefinite nature which the halogens form with sulfur.

The oxidation-reduction potentials given above were measured in each case between a saturated calomel electrode and a platinum electrode. The value of the "oxidation-reduction potential" as used herein and in the claims is to be read as including determination of the potential of the bath liquid employed with these or with equivalent electrodes. The term, "oxidation-reduction potential" as used herein is defined in pages 246-249 of "Principles and Applications of Electrochemistry," volume 1, by Creighton, published by Wiley, 1935.

The quantity of insoluble sulfur present in the solid sulfur can be increased if one adds to the sulfur before quenching, a small quantity of a halogen such as chlorine, bromine or iodine. From 0.1% to 0.3% by weight usually suffices and one should not use too large a quantity as this has the opposite effect. If this is done, the quantity of insoluble sulfur present is increased, other things remaining constant, by about 10%. Thus, if under a given set of conditions and with a given bath, one secured a product containing 60% insoluble sulfur, this quantity can be increased to a value of the order of 70% by including a small quantity of a halogen or a material providing free halogen such as sulfur chloride. The halogen also assists in stabilizing the insoluble sulfur in the product against reversion to the soluble form.

The product is preferably dried at a temperature elevated with respect to a normal atmospheric temperature. This hastens hardening of

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the product and, in addition, stabilizes the insoluble sulfur against reversion at normal atmospheric temperatures to the soluble form, particularly if a halogen is not present. The heating is preferably carried on at temperatures in the range of about 30° to about 80° C., although intermediate temperatures (40°-70° C.) can be employed. Retention at 50°-60° C. for one to two hours usually suffices. The exact time cannot be given since it is difficult to measure the true temperature of a mass of this character; also the heat imparting ability of equipment varies. Generally, a few hours suffice. When the sulfur is returned to normal atmospheric temperature, its rate of reversion is materially lowered and it can thereafter be extracted with a solvent such as carbon bisulfide, benzene, toluene or xylene to give a material substantially all of which is insoluble in carbon bisulfide and is stable.

The control of oxidation-reduction potential is most effective when utilized in the quenching of sulfur vapor. An increased yield of insoluble sulfur is also obtained when sulfur is quenched from a temperature of about 250° C. and higher as a liquid or as a mixture of sulfur vapor and liquid sulfur at a temperature of about 250° C. and higher, or as a vapor at 400° C. and above.

To illustrate practice of the invention, the following examples are set forth:

Example 1

Sulfur was vaporized at the rate of 500 pounds per hour. The sulfur vapor, at a temperature of 500° C., was introduced below the surface of an aqueous acidic body comprising 1000 gallons in volume and consisting of an 0.1 normal solution of sodium sulfite containing 18% hydrochloric acid. The oxidation-reduction potential of the bath was 0.320 volt. The bath was circulated through a cooler to maintain its temperature at approximately 20° C. The oxidation-reduction potential of the bath was metered constantly by measuring the potential of the liquid passing to the cooler and about 0.5 cubic foot per hour of SO₂ was introduced into the bath as make-up to maintain the quantity of sodium sulfite in the bath and to maintain the potential above 0.3 volt and in the desired range. The sulfur recovered contained 45% insoluble in carbon bisulfide.

Example 2

Under the same conditions as in Example 1, but by utilizing an aqueous acidic bath containing sufficient potassium chlorate to be 0.1 N and 5.0% nitric acid, a condensed sulfur product was obtained containing 48.5% of sulfur insoluble in carbon bisulfide. The potassium chlorate was added as a 5% solution and at the rate of about 15 cc. per minute to maintain the oxidation-reduction potential at 0.54 volt.

Example 3

Under the same conditions as in Example 1, but utilizing an aqueous acidic bath containing 5.0% nitric acid and 0.2% of ferric iron, present as ferric chloride, a condensed sulfur product was obtained containing 55% of sulfur insoluble in carbon bisulfide. During the quenching of the sulfur vapor, the oxidation-reduction potential was maintained at 0.64 volt by controlled aeration of the bath with compressed air.

Example 4

Under the same conditions as in Example 1,

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but utilizing an aqueous acidic bath containing 0.4% ferric iron and 2% nitric acid, a condensed sulfur product was obtained containing 61% of sulfur insoluble in carbon bisulfide. During the quenching of the sulfur vapor, the oxidation-reduction potential was maintained at 0.74 volt by controlled aeration of the bath with compressed air.

Example 5

Under the same conditions as in Example 1, but utilizing an aqueous acidic bath containing 2 of ferric acid and 5% of nitric acid, a condensed sulfur product was obtained containing 51.5% of sulfur insoluble in carbon bisulfide. During the introduction of the sulfur vapor, the oxidation-reduction potential was maintained at 0.83 volt by controlled aeration of the bath with compressed air.

Example 6

Under the same conditions as in Example 1, but utilizing an aqueous acidic bath containing sufficient potassium permanganate to be 0.1 N and 5% HNO₃, a condensed sulfur product was obtained containing 48.5% of sulfur insoluble in carbon bisulfide. The potassium permanganate was added as a 5% solution at the rate of about 40 cc. per minute to maintain the oxidation-reduction potential at 1.19 volts.

As an oxidizing material, one can employ water soluble manganic salts, in addition to those previously mentioned, to oxidize the reducing substances introduced into the bath by the stream of sulfur vapor and which, unless oxidized, lower the oxidation-reduction potential until it is outside of the preferred potential range, and concurrently reduce the insoluble sulfur content of the product. Those skilled in the art can readily make up various acidic aqueous baths having a potential in the desired range and can employ various oxidizing materials to oxidize the reducing substances at a rate sufficient to maintain the bath at a desired potential. The quantity of oxidizing material to be added to the bath depends upon the quantity of impurities present in the sulfur. A crude sulfur will generally require the addition to the bath of a greater quantity of an oxidizer than will a refined sulfur. Since the potential of the bath can be measured continuously, it is an easy matter to adjust the rate of addition of the oxidizer to that required to maintain a given potential for a given rate of injection of a given sulfur.

This is a continuation in part of my application Serial Number 587,823, filed April 11, 1945, which in turn is a continuation in part of my application Serial Number 513,997, filed December 11, 1943, and each of which is now forfeited.

I claim:

1. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor into a cold aqueous bath having an oxidation-reduction potential between 0.3 volt and 1.2 volts throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing salt to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.3 volt and 1.2 volts.

2. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor into a cold aqueous bath having an oxidation-reduction potential between 0.6 volt and 0.83 volt

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throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing salt to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.6 volt and 0.83 volt.

3. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor into a cold aqueous bath having an oxidation-reduction potential between 0.67 and 0.77 volt throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing salt to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.67 volt and 0.77 volt.

4. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor into a cold aqueous bath having an oxidation-reduction potential between 0.3 volt and 1.2 volts throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing material to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.3 volt and 1.2 volts.

5. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor into a cold aqueous bath having an oxidation-reduction potential between 0.6 volt and 0.83 volt throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing material to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.6 volt and 0.83 volt.

6. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor into a cold aqueous bath having an oxidation-reduction potential between 0.67 and 0.77 volt throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing material to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.67 volt and 0.77 volt.

7. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor at a temperature of at least 250° C. into a cold aqueous bath having an oxidation-reduction potential between 0.3 volt and 1.2 volts throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing material to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.3 volt and 1.2 volts.

8. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor at a temperature of at least 250° C. into a cold aqueous bath having an oxidation-reduction potential between 0.6 volt and 0.83 volt throughout the process to quench and condense said sulphur vapor within said bath to a solid and adding to said bath sufficient of an oxidizing material to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.6 volt and 0.83 volt.

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9. A process for producing sulphur which is insoluble in carbon bisulphide comprising continuously introducing a stream of sulphur vapor at a temperature of at least 250° C. into a cold aqueous bath having an oxidation-reduction potential between 0.67 and 0.77 volt throughout the process to quench and condense said sulphur vapor within said bath to a solid, and adding to said bath sufficient of an oxidizing material to maintain said bath during the quenching of the sulphur at an oxidation-reduction potential between 0.67 volt and 0.77 volt.

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REFERENCES CITED

The following references are of record in the file of this patent:

- 5 Gal: Comptes Rendus, vol. 114, pp. 1183-4 (1892), and vol. 116, pp. 1373-5 (1893).
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