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Sanders

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[54] **DESULFURIZATION OF COAL**

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[52] **U.S. Cl.** ..... **44/1 R**

[51] **Int. Cl.²** **C10L 5/00**

[58] **Field of Search** ..... 44/1 R; 201/17; 75/6

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[57] **ABSTRACT**

A process is disclosed for desulfurization of coal which comprises: digesting, in a digestion zone, coal and a Group IA or IIA metal oxide or mixtures thereof in the presence of a fused metal chloride salt medium, which medium is capable of dissolving sulfur-containing organic compounds present in the coal and which has a melting point below the digestion temperature; passing anhydrous hydrogen chloride into the digestion zone and removing from the digestion zone desulfurized coal. Subsequent refining of the desulfurized coal is also disclosed.

21 Claims, No Drawings

DESULFURIZATION OF COAL

BACKGROUND OF THE INVENTION

It is estimated that by **1975** the U.S. will have a coal production ranging from **600** to **800** million metric tons. The majority of this coal, about **70** percent, will be burned directly for the generation of electricity and steam power, for comfort heat, for metallurgical processes and for the firing of ceramic productions. Since almost all coal contains both organic and inorganic sulfur compounds, the polution burden placed on the environment upon burning the coal can be quite large as the burning produces sulfur oxides which are contaminants. For example, a one-million kilowatt power plant (which is not unusually large) burning coal containing **3.5** percent sulfur (which is not unusually high) emits sulfur oxides equivalent to about **1,000** tons of sulfuric acid per day. From these facts it can be seen that the usefulness of coal for its energy value is somewhat tempered by the polution problems attenuant with its use. There are many studies now being made on an international scale for solving the coal polution problem. Some efforts are directed towards cleaning up the stack gasses from the coal-burning furnaces. The stack gas directed solutions are generally hampered by huge capital outlays. Other solutions which would not require such capital outlays are those directed towards the desulfurization of coal prior to its burning. To date no generally known economical desulfurization process has been developed.

It is therefore an object of this invention to provide a process for the desulfurization of coal which is relatively uncomplicated and which is economically attractive.

THE INVENTION

This invention relates to a process for the desulfurization of coal which contains pyritic sulfur and sulfur-containing organic compounds comprising: digesting, in a digestion zone, the coal and a Group IA or IIA metal oxide salt or mixtures thereof in the presence of a fused metal chloride salt medium, which medium is capable of dissolving sulfur-containing organic compounds present in the coal and which has a melting point below the digestion temperature, until at least part of the dissolved sulfur-containig organic compounds and pyritic sulfur has been converted to Group IA or IIA metal sulfides; feeding anhydrous hydrogen chloride to the digestion zone subsequent to the digestion period to convert the formed Group IA or IIA metal sulfides to Group IA or IIA metal chlorides respectively and hydrogen sulfide; and removing from the digestion zone an at least partially molten mixture containing desulfurized coal, the formed Group IA or IIA metal chloride salts and the metal choride salt medium. Digestion temperatures are within the range of from about **400°** to about **600°C**. Pressures for the digestion are generally atmospheric and are not critical to the process. percent

The fused metal chloride salt medium can be either a single metal chloride salt or a mixture of such salts. As before said, the fused metal chloride salt medium must have a melting point below the digestion temperature and be capable of dissolving sulfur-containing organic compounds found in the coal. The extent of the solubility of the sulfur-containing organic compounds in the fused salt medium should be to the extent that at least **50** percent of the original sulfur-containing organic compounds in the coal will be dissolved.

Examples of the single metal chloride salts which may be utilized as the medium are manganese chloride, ferric chloride, cupurous chloride, zinc chloride, stannous chloride, bismuth trichloride, cadmium chloride and the like. Exemplary of mixtures of metal chloride salts useful for the purpose of this invention are sodium chloride-manganese chloride, ferric chloride-cobalt dichloride, cupuric chloride-zinc chloride, zinc chloride-lead dichloride, etc. The exact proportions of the salts making up the mixtures will, of course, be determined by the resulting melting point of the mixtures which point must be below the digestion temperature.

As the high solubility in alcohol of the metal chloride salts making up the medium will be highly desirable for subsequent refining of the desulfurized coal, as hereinafter described, salts, whether they be used singularly or in mixtures, such as manganese chloride, ferric chloride, zinc chloride, stannous chloride, and bismuth trichloride are preferred. Of these preferred salts, the most preferred salt is zinc chloride due to its availability and low cost. Preferred mixtures of salts are zinc chloride-ferric chloride and zinc chloride-calcium chloride.

The Group IA and IIA metal oxide salts utilized in the process of this invention are most preferably anhydrous. The absence of water in these salts is important from a safety standpoint as popping and spattering of the hot digestion mixture will be prevented. Examples of Group IA or IIA metal oxide salts which may be used in this invention are sodium oxide, magnesium oxide, calcium oxide, potassium oxide, cesium oxides, etc. Mixtures of these salts may, of course, be used. The preferred metal oxides are calcium oxide and sodium oxide as they are extremely economical reactants. Of these preferred salts, calcium oxide is most preferred.

The digestion temperature should be within a range of from about **400°** to about **600°C**. Selection of temperatures within this range will be dependent to some extent upon the particular type of coal being desulfurized as different coals have different temperatures at which serious thermal deterioration occurs. These deterioration temperatures are, of course, to be avoided. For example, temperatures below **550°C** should be utilized for some bituminous coals. Temperatures around **400°–450°C** should be used for the lignites. Anthracite coal can withstand temperatures in the region of **500°** to **550°C**.

The digestion period should be that period of time which is sufficient to achieve at least substantially complete reaction of the organic sulfur compounds in solution and of the pyritic sulfur. Generally speaking, times ranging from one-fourth to **5** hours are sufficient with the time being dependent upon the amount of organic sulfur compounds and pyritic sulfur present and the type of coal being treated. From two to three hours have been found to be sufficient for coal which contains up to about **1.0** percent organic sulfur compounds and about **0.2** percent pyritic sulfur.

Quantitatively, the amount of Group IA or IIA metal oxide salt utilized will be that amount which provides at least a stoichiometric mole ratio of these salts to the sulfur present in the pyritic sulfur and in the dissolved organic sulfur compounds. In other words, when utilizing Group IA metal oxide salts a mole ratio of this salt to the sulfur should be at least **2:1**. When utilizing

Group IIA metal oxide salts a mole ratio of **1:1** is sufficient. Amounts less than stoichiometric may be utilized, however such amounts do not result in high reaction efficiency. Amounts in excess of stoichiometric can also be used. In fact, mole ratios up to **4:1** for Group IA metal oxide salts and up to **2:1** for Group IIA metal oxide salts are preferred as reaction kinetics are improved by the presence of the excess of these salts. For calcium oxide, a highly preferred salt, it has been found that a mole ratio of from about **1.2:1** to **1.5:1** is most preferred.

The amount of metal chloride salt used as the medium should be that amount which will result in a relatively liquid digestion mixture. Generally speaking, such a mixture can be achieved by utilizing the salt medium in an amount so that the weight ratio of medium to coal and metal oxide salt is within the range of from about **6:1** to about **2:1.**

The coal, prior to digestion, should be prepared by grinding so that it will at least pass through a ½-inch mesh. This grinding of the coal is to hasten the dissolving of the sulfur-containing compounds in the fused metal chloride salt medium. The anhydrous hydrogen chloride fed to the digestion zone subsequent to the digestion period can be achieved by bubbling the gaseous acid through the digestion mixture, i.e., a mixture containing fused metal choride salt, coal and Group IA or IIA metal sulfides and remaining oxide salt. The amount of anhydrous hydrogen chloride used should be at least stoichiometric with relation to the amount of Group IA or IIA metal sulfides formed by the digestion. Amounts in excess of stoichiometric are, however, preferred. Amounts ranging up to **100** times stoichiometric quantities are most preferred. By passing the anhydrous hydrogen chloride through the digestion mixture the Group IA and IIA metal sulfides are converted to Group IA or IIA metal chlorides, respectively, with the evolution of gaseous H_2S from the digestion zone. The H_2S can either be disposed of or can be utilized in processes having an H_2S demand.

After the anhydrous hydrogen chloride has been fed to the digestion zone the at least partially molten material remaining in the zone is removed therefrom. The remaining material includes for the most part desulfurized coal, the metal chloride salt used as the medium and the formed Group IA or IIA metal chlorides. Small amounts of Group IA or IIA metal oxides and sulfides may also be present. If it is desired, further refining of this material to cleanse the desulfurized coal of the greater portions of these various salts and reaction products may be effected.

One refining technique comprises: cooling the removed at least partially molten material so as to solidify the molten components; crushing the solidified material; extracting from the crushed material, with alcohol, at least part of the metal chloride salt used as the medium and the formed Group IA or IIA metal chlorides; and separating the desulfurized coal from the alcohol-salt solution. Optionally, the desulfurized coal may be even further refined by contacting the desulfurized coal with a dilute aqueous acid to extract any remaining salts or metal sulfides and separating the coal from the dilute aqueous acid-salt-sulfide solution. The recovered desulfurized coal can then be dried and pelletized to a form for consumption.

Cooling of the removed material is necessary to get it in a slag form, i.e., an all solid form, which is suitable for further processing. As alcohol is to be utilized later in the refining scheme, the material should be cooled so that it has a temperature lower than the boiling point of the alcohol to be used. This cooling can be achieved by placing the material in a cooled vessel until it has reached the desired temperature.

After the material has been cooled it is desirable that it be crushed so that it will have a size which is favorable to the kinetics of extraction and which allows for easy handling. Generally speaking the material should be crushed so that is can pass through a ½-inch or ¼-inch mesh. Crushing can be achieved by passing the material through a ball mill or a roller mill.

The crushed material is then subjected to alcohol extraction to remove the metal chloride salt which was used as the medium and the formed alkali or alkaline earth metal salts. Various alcohols can be utilized, for example, methanol, ethanol, butanol, isopropanol, pentanol, tertiary butanol, propanol, etc., are all useful. This extraction can be achieved by merely placing the crushed material in an alcohol bath with stirring.

The extraction with alcohol of the various mentioned salts from the crushed material permits a variation in the process of this invention. It is possible — indeed sometimes desirable to contact the crushed material with an alcohol-hydrogen chloride solution. By so doing, the introduction of anhydrous hydrogen chloride to the digestion zone may be eliminated. The hydrogen chloride in the alcohol will perform the same function as the anhydrous hydrogen chloride feed to the digestion zone. In other words, the hydrogen chloride in the alcohol solution will react with the formed Group IA or IIA metal sulfides to yield Group IA or IIA metal chlorides, respectively, with the evolution of hydrogen sulfide. The alcohol will then act to dissolve these formed chlorides so that they may be extracted from the desulfurized coal. The amount of HCl used with the alcohol is the same as the amount used in the first described embodiment where anhydrous HCl is fed to the digestion zone.

After extraction the alcohol and its dissolved salts are removed from the solid desulfurized coal. This can be achieved by any of the well-known solid-liquid separations known to those skilled in the art. For example, filtration, centrifuging, decantation, etc., can be used.

The alcohol-salt solution can be optionally fed to distillation so that the alcohol may be distilled from the salts and recycled back to the extraction step. The salts which have been separated from the alcohol can be recycled to the digestion zone.

The desulfurized coal which has been separated from the alcohol-salt solution will still contain small amounts, i.e., less than **5** weight percent, of the metal chloride salts medium and Group IA or IIA metal sulfides, chlorides and oxides. Optionally, these small amounts of impurities can be reduced by contacting the desulfurized coal with a dilute aqueous acid, e.g., a five percent hydrogen chloride solution. Filtration is then utilized to recover the desulfurized coal. The recovered desulfurized coal can then be dried with heat and may be further pelletized so as to achieve a desirable commercial form.

The process of this invention may be utilized to desulfurize many types of coal. For example, it may be utilized to desulfurize anthracite, bituminous, subbituminous, and lignite types of coal. The sulfur-containing organic compounds found in these types of coal generally are organic compounds which have **a**

carbon-sulfur-carbon bond or a carbon-sulfur-sulfur-carbon bond in their structure.

The following non-limiting examples will further illustrate the process of this invention. The equipment used in each example was essentially the same. The digestion reactor consisted of a small vertical muffle furnace lined with a graphite sleeve. Inside of the sleeve was placed a glass reactor tube in which the digestions were to take place. Temperatures were controlled by way of a thermacouple placed in a glass tube which was inserted into the digestion zone. A glass dip tube was inserted into the glass reactor tube to provide a mode for anhydrous hydrogen chloride addition. A T-shaped glass tube was placed into the digestion zone to allow for a nitrogen purge during digestion. The acid and alcohol extraction were performed either in beakers or in extraction thimbles.

EXAMPLE I

A metallurgical coal containing from about **1.0** to about **1.2** percent total sulfur was crushed to a **−1–4** inch size. Six grams of the coal, along with **30** grams of zinc chloride and **3** grams of calcined lime were heated together in the digestion zone to a temperature of **450°C** for **2** hours. After this period anhydrous hydrogen chloride was bubbled through the glass dip tube for one-half hour. The resultant mass was then dumped from the digestion zone and cooled. The cooled material was ground to about **−16** mesh and extracted with isopropanol in a beaker for about three-fourths of an hour. The resultant mass was separated from the isopropanol-salt solution and contacted with **5** percent aqueous hydrogen chloride solution for one hour. The remaining solids were filtered from the acid solution and dried by heating. It was found by X-ray fluorescence that **62.1** percent of the total sulfur had been removed from the coal.

EXAMPLE II

The coal of Example I was used for Example II. Twenty-five grams of zinc chloride, **3** grams of lime and **5** grams of the coal were heated together in a digestion zone to a temperature of **500°C** for **2½** hours. After this period anhydrous hydrogen chloride was bubbled through the glass dip tube for one hour. The resultant mass was then dumped from the digestion zone and cooled. The cooled material was ground to about **−16** mesh and extracted with methanol for **2** hours. X-ray fluorescence showed that **54.6** percent of the original sulfur present was removed.

EXAMPLE III

Five grams of the coal, **25** grams of zinc chloride and **3** grams of lime were heated together in the digestion zone to a temperature of **400°C** for **3¼**hours. After this period anhydrous hydrogen chloride was bubbled through the glass dip tube for one-half hour. The resultant mass was dumped from the digestion zone and cooled. The cooled material was ground to about **−16** mesh and extracted with methanol for about **2** hours. X-ray fluorescence showed that **64.6** percent of the original sulfur present had been removed.

I claim:

1. A process for the desulfurization of coal which contains pyritic sulfur and sulfur-containing organic compounds comprising:

a. digesting, in a digestion zone, the coal and a Group IA or IIA metal oxide salt or mixtures thereof in the presence of a fused metal chloride salt medium, which medium is capable of dissolving at least **50** percent of the sulfur-containing organic compounds present in the coal and which has a melting point below the digestion temperature, until at least part of the pyritic sulfur and the dissolved sulfur-containing organic compounds have been converted to Group IA or IIA metal sulfides; said metal oxide salt or mixtures thereof being present in an amount which provides at least a stoichiometric mole ratio of said metal oxide salt to the amount of sulfur present in said pyritic sulfur and said dissolved organic compounds, said fused metal chloride salt medium being present in an amount which will result in a relatively liquid digestion mixture;

b. feeding anhydrous hydrogen chloride to the digestion zone subsequent to the digestion period to convert the formed Group IA or IIA metal sulfides to Group IA or IIA metal chlorides respectively and hydrogen sulfide; and

c. removing from the digestion zone an at least partially molten mixture containing desulfurized coal, the formed Group IA or IIA metal chloride salts and the metal chloride salt medium.

2. The process of claim **1** wherein the metal oxide salt is calcium oxide or sodium oxide.

3. The process of claim **1** wherein the metal oxide salt is calcium oxide.

4. The process of claim **1** wherein the metal chloride salt medium is zinc chloride, a mix of zinc chloride and ferric chloride or a mix of zinc chloride and calcium chloride.

5. The process of claim **1** wherein the metal chloride salt medium in zinc chloride.

6. The process of claim **1** wherein the desulfurized coal in the molten mixture is separated from at least part of the formed chloride salts and the metal chloride salt medium by a refining process which comprises:

a. cooling the removed at least partially molten material so as to solidify the molten components;

b. crushing the solidified material;

c. extracting from the crushed material with alcohol at least part of the metal chloride salt used as the medium and the formed Group IA or IIA metal chlorides; and

d. separating the desulfurized coal from the alcohol-salt solution.

7. The process of claim **6** wherein the separated desulfurized coal is further refined to reduce the content of any remaining metal chloride salt medium and Group IA or IIA metal sulfides or chlorides by a second refining process which comprises:

a. contacting the separated desulfurized coal with a dilute aqueous acid to extract at least part of the remaining metal chloride salt medium and the remaining Group IA or IIA metal sulfides or chlorides in the separated desulfurized coal;

b. separating the contacted desulfurized coal from the resultant dilute aqueous acid-metal chloride salt-sulfide solution; and

c. drying and pelletizing the dsulfurized coal from Step (b).

8. The process of claim **6** wherein the metal oxide salt is calcium oxide or sodium oxide.

9. The process of claim 6 wherein the metal oxide salt is calcium oxide.

10. The process of claim 6 wherein the metal chloride salt medium is zinc chloride, a mix of zinc chloride and ferric chloride or a mix of zinc chloride and calcium chloride.

11. The process of claim 6 wherein the metal chloride salt medium is zinc chloride.

12. A process for the desulfurization of coal which contains pyritic sulfur and sulfur-containing organic compounds comprising:

a. digesting, in a digestion zone, the coal and a Group IA or IIA metal oxide salt or mixtures thereof in the presence of a fused metal chloride salt medium, which medium is capable of dissolving at least 50 percent of the sulfur-containing organic compounds present in the coal and which has a melting point below the digestion temperature, until at least part of the pyritic sulfur and the dissolved sulfur-containing organic compounds have been converted to Group IA or IIA metal sulfide; said metal oxide salt or mixtures thereof being present in an amount which provides at least a stoichiometric mole ratio of said metal oxide salt to the amount of sulfur present in said pyritic sulfur and said dissolved organic compounds, said fused metal chloride salt medium being present in an amount which will result in a relatively liquid digestion mixture;

b. removing from the digestion zone an at least partially molten mixture containing desulfurized coal, the formed Group IA or IIA metal sulfide and the metal chloride medium;

c. cooling the removed at least partially molten material so as to solidify the molten components;

d. crushing the solidified material;

e. contacting the crushed material with an alcohol-hydrogen chloride solution so as to convert the formed Group IA or IIA metal sulfides to Group IA or IIA metal chlorides respectively and hydrogen sulfide, and to extract from the desulfurized coal at least part of the metal chloride salt used as the medium and the formed Group IA or IIA metal chlorides; and

f. separating the desulfurized coal from the alcohol-salt solution.

13. The process of claim 12 wherein the separated desulfurized coal is further refined to reduce the content of any remaining metal chloride salt medium and Group IA or IIA metal chlorides or sulfides by a second refining process which comprises:

a. contacting the separated desulfurized coal with a dilute aqueous acid to extract at least part of the remaining metal chloride salt medium and the remaining Group IA or IIA metal sulfides or chlorides in the separated desulfurized coal;

b. separating the contacted desulfurized coal from the resultant dilute aqueous acid-metal chloride salt-sulfide solution; and

c. drying and pelletizing the desulfurized coal from Step (b).

14. The process of claim 12 wherein the metal oxide salt is calcium oxide or sodium oxide.

15. The process of claim 12 wherein the metal oxide salt is calcium oxide.

16. The process of claim 12 wherein the metal chloride salt medium is zinc chloride, a mix of zinc chloride and ferric chloride or a mix of zinc chloride and calcium chloride.

17. The process of claim 12 wherein the metal chloride salt medium is zinc chloride.

18. The process of claim 1, wherein when said metal oxide salt is a Group IA metal oxide salt, the mole ratio of said salt to said sulfur ranges from about 2:1 to about 4:1; and when said metal oxide salt is a Group IIA metal oxide salt, the mole ratio of said salt to said sulfur ranges from about 1:1 to about 2:1.

19. The process of claim 1, wherein said fused metal chloride salt medium is present in a weight ratio range of said medium to said coal and said metal oxide salt of from about 6:1 to about 2.1.

20. The process of claim 12, wherein when said metal oxide salt is a Group IA metal oxide salt, the mole ratio of said salt to said sulfur ranges from about 2:1 to about 4:1; and when said metal oxide salt is a Group IIA metal oxide salt, the mole ratio of said salt to said sulfur ranges form about 1:1 to about 2:1.

21. The process of claim 12, wherein said fused metal chloride salt medium is present in a weight ratio range of said medium to said coal and said metal oxide salt of from about 6:1 to about 2:1.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,909,213

DATED : September 30, 1975

INVENTOR(S) : Robert N. Sanders

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 59, "percent" should be omitted. Column 5, line 56, "3-1/4 hours" should read -- 2-1/4 hours -- . Column 6, line 37, "in" should read -- is -- . Column 8, line 35, "2.1" should read -- 2:1 -- . Column 8, line 41, "form" should read -- from -- .

Signed and Sealed this

sixteenth Day of *December 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks