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MANUFACTURE OF ALKALI AND ALKALINE EARTH METAL SULFIDS,
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1,212,702.

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3 SHEETS-SHEET 2.
To all whom it may concern:

Be it known that we, HEINRICH SPECKETER and WILLHELM HOFMANN, subjects of the German Emperor, and residents of Griesheim-on-the-Main, Germany, have invented certain new and useful Improvements in and Connected with the Manufacture of Alkali and Alkaline-Earth Metal Sulfids, of which the following is a specification.

The object of this invention is to provide an economical and efficient process for the manufacture of alkali sulfids and alkaline earth sulfids by blowing with air mixtures of carbonaceous matter and sulfates, or bisulfates, of alkali, or of alkaline earth, in a shaft furnace, in which air supply can be regulated. Hitherto the only process which has been practically employed for the manufacture of the said sulfids consists in heating the corresponding sulfates in a reverberatory furnace with a large excess of coal to absorb the resulting fusible sulfur compounds, so as to prevent the material of the furnace from being attacked, oxidation by air being prevented. A process is described in the specification of the German Patent No. 196,606, in which sodium sulfide containing 90 per cent. of Na₂S₅ is obtained by melting sulfuret of sodium and allowing it to run over electrically heated coke, but the cost of the electric energy is a disadvantage, as electric machines absorb about 20 per cent. of the heat energy of the fuel and electric furnaces are only advantageous for very high temperatures. Such processes have hitherto aimed at avoiding access of air to the mixture of coal and sulfate, because it was feared that the sulfid might be again oxidized, if air were present. The application of an electric furnace is only to be resorted to for temperatures of above 1000° centigrade. A further process for the manufacture of sulfids is described in U. S. Patent No. 174,441 to Hasenbach according to which a finely pulverized mixture of coal and sulfate is heated, but it involves the use of a reverberatory furnace, and its attendant evils, and it has only for its object to make a product which is granular like the initial material, and is not melted, or sintered. It has also been proposed to use shaft furnaces but in a way which cannot be carried out in practice, or at any rate does not offer any advantage over the use of reverberatory, or muffle, furnaces, and these processes have not supplanted the employment of reverberatory furnaces, and the most recent suggestions for improvements have been based on the use of reverberatory furnaces. Among the processes which employ a shaft furnace is one proposed by Wilson, (see British Patent 1361 of 1859) in which the sulfate is made molten in a shaft furnace and is caused to flow through a column of coke, heated to a bright red heat by a lateral gas producer. Claus has proposed an improvement on this process, which improvement consists in causing the molten sulfate to flow through a column of coke heated to a bright red heat in a shaft furnace (see the specifications of British Letters Patents No. 819 and 2616 A. D. 1869). But none of them describe any means by which in the manufacture of sulfids from sulfates the known disadvantages of a shaft furnace as regards an oxidizing action of the air blast and a destruction of the furnace walls are avoided. Weldon has proposed a process in which the sulfate is first melted and then caused to run over coal heated in a revolving furnace, air being carefully excluded.

The process which constitutes our present invention has the great advantage over the aforesaid prior processes that its operation is continuous and much more economical and the hereinbefore mentioned disadvantages are avoided. It is carried out as follows:—The furnace is preferably one having a water-jacket and is provided with regulatable twyer's. It is filled with large pieces of carbonaceous matter, such as coal, or coke, the ash content of which is preferably low so as to avoid, as much as possible, impurities in the melt. The supply of air is so regulated by adjusting the twyers, that there is constantly a red heat throughout the furnace, this being an important feature of the present invention. The sulfate, or bisulfate, mixed with a suitable quantity of carbonaceous matter such as coal is then charged into the furnace. The coal, or the like, added to the sulfate, or bisulfate, is in sufficient excess (for example 240 parts of sulfate are mixed with 100 parts of carbon-
aceous matter) to subsequently reduce the last traces of unreduced sulfate, or bisulfate, which may remain in the tapped off melt and to cause the melt to be loosened by the gases produced. The salt melts and runs over the heated and glowing carbonaceous matter such as coal, or coke, and, at about 1000° centigrade, is reduced according to the equation

$$\text{Na}_2\text{SO}_4 + 4\text{C} = \text{Na}_2\text{S} + 4\text{CO}.$$  

The escaping carbon monoxid passes in a direction opposite to that of the sinking sulfate, or bisulfate, and reduces the sulfate or bisulfate, as follows:

$$\text{Na}_2\text{SO}_4 + 4\text{CO} = \text{Na}_2\text{S} + 4\text{CO}_2$$

so that the process is accelerated. A part of the carbon monoxid escapes and can be utilized in any required manner, for instance for heating the air from the blowing apparatus. The melt flows down and can be removed either continuously, or be tapped off from time to time. It contains, in addition to coal, or like, dust, the ash of the carbonaceous matter such as coal, or coke.

The improved process has the advantage over all those hitherto used, or proposed, that it requires a much smaller amount of carbonaceous matter, such as coal, and no great amount of charge in the furnace at one time, so that heavy repairs are not necessary and the cost of manufacture is considerably decreased. That is the coal, for example, introduced into the furnace constitutes both the means for furnishing the required heat and also that for converting the sulfate, thus saving the amount of fuel consumed in and serving no other purpose than for heating the furnace externally. The melt obtained, which contains about 85 per cent. of the sulfid, can be used as obtained in the form of large pieces, or it can be finely pulverized, for example in a ball mill (air being excluded) in order to obtain a homogeneous powder.

If crystallized sulfids be required the melt is allowed to flow directly from the furnace into water and the hot saturated solution obtained is quickly filtered and the crystals are separated in a cold stirring vessel. The mother lye and the wash-water can be used again for dissolving further melts. It is preferable, in carrying out these operations, to prevent the access of air, as thereby the wasteful conversion of the sulfid, into carbonates, thiosulfates, and like oxidation products, is avoided. The use of a water-jacketed furnace has the advantage that the walls of an iron furnace can, without the use of a lining, be protected by simple water cooling against any destructive action by the sulfid which is formed.

Although the advantages of shaft furnaces for metallurgical and other chemical purposes has long been known to the expert, such furnaces have hitherto not been used in the manner, and for the purpose, herebefore described.

In the drawing Figure 1 is an outer view 7 of a shaft furnace which may be used for carrying out the process described. Fig. 2 is a vertical section on the line 1—1 of Fig. 1 and Fig. 3 a vertical section on the line 2—2 of Fig. 2.

The shaft furnace consists of two parts a and b. The upper part a is of masonry and is independently supported on iron columns c. The lower part b consists of a hollow iron case with a water-jacket d. The iron case may be lined with brickwork e which may, as shown in Figs. 2 and 3, extend up into the part a. It rests on adjustable supports f. The furnace is filled through the side-opening g and the gases escape through the central opening h. The melt runs off through the tap-hole i. The blast air is fed by the common conduit k to the twyers l. Each of the twyers is provided with regulating taps m, by which the quantity of air supplied can be controlled.

We claim:

1. The herein described improvement in the method of manufacturing alkali-metal sulfids by heating a mixture of carbonaceous material and an alkali metal sulfate consisting in providing in the mixture an amount of carbonaceous material in sufficient excess of that consumed in the melting operation to subsequently reduce any 10% unreduced sulfate or bisulfate which may remain in the melt.

2. The herein described method of manufacturing alkali-metal sulfids comprising heating in a shaft furnace a mixture of carbonaceous material and an alkali-metal sulfate while introducing air to the furnace under such control that it will maintain combustion of the carbonaceous material without causing oxidation of the sulfid produced thereby, the amount of carbonaceous material in the mixture being such that a portion thereof will pass off in the melt.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

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WILHELM HOFMANN.

Witnesses:
FRANZ HASSLACHER,
ERWIN DEBBRETY.