This invention relates to improvements in the production of sodium sulfide from sodium sulfate.

The reduction of sodium sulfate to sodium sulfide is usually carried out either with coal or with reducing gases. When reducing with coal the operation is carried out at temperatures of about 1000° C. in flame furnaces, shaft furnaces or rotary tubular furnaces, and a crude melt is obtained which contains, besides sodium sulfide, also sulfate, sulfite, thiosulfate, soda and, as an insoluble residue, ash and unburnt coal. A commercial product is not obtained until the melt has been dissolved and the resulting solution has been clarified and concentrated. A particular drawback of the said process is the low stability of the furnace linings by reason of the action of the strongly corrosive sodium sulfide melt. This drawback is avoided by employing reducing gases instead of coal, for example the most lightly reacting hydrogen. The most favorable reaction temperature in this case is about 700° C. In this way a commercial sodium sulfide can be obtained from sodium sulfate by a one stage operation, and moreover at the low reaction temperature which permits working in the absence of the fused state, a long life of the furnace is ensured. A drawback of the process however is its dependence on the use of additions which are made in order to accelerate the reaction speed and which pass into the final product. The following have been proposed as catalysts: caustic soda, sulfur, carbon, metals, such as iron, nickel, chromium and copper, and mixtures of the said metals with molybdenum, tungsten, uranium, titanium, thorium, arsenic, antimony, bismuth or phosphorus. While sodium sulfate melts at about 880° C. and sodium sulfide not until about 1180° C., the melting points of mixtures of sulfate and sulfide are considerably lower, at about 620° to 750° C., and in the case of incomplete and slow reduction there are obtained viscous melts which are deprived of further reaction with the reducing gases sweeping thereover. The reaction speed must therefore be so increased by the addition of an active catalyst that the fusion temperature of the sulfate-sulfide mixture corresponding to the reaction temperature attained, is always somewhat higher than the latter.

In practice on a technical scale heavy metal compounds, in particular those of iron, are mainly used as catalysts; they impart to the sodium sulfide a dark, unpleasant appearance and are troublesome in many of the purposes for which the sodium sulfide is used, as for example in the production of dyestuffs. We have now found and this constitutes the object of our invention, that a high percentage, almost colorless sodium sulfide is obtained by carrying out the reduction of sodium sulfate with reducing gases in the presence of subordinate amounts of sodium salts of organic acids, in particular aliphatic acids, as for example sodium formate and sodium acetate. The sodium salts of aliphatic acids having more than one carboxylic group, as for example sodium oxalate and sodium tartrate, have proved to be especially suitable. Though carboxylic acids having more than 5 C atoms may be also used we prefer to use salts of such acids as contain up to 5 C atoms for economical reasons. Additions of about 1 to 5 per cent, with reference to the sodium sulfate, are usually sufficient.

The tendency of mixtures of sulfate and sulfide to exhibit agglutination phenomena far below the melting point of the individual salts, is substantially suppressed by the said additions, and the reduction can be carried out without trouble in the temperature range of 660° to 800° C. When working in a rotary tubular furnace, the sodium sulfide is obtained in a conveniently employable granular form.

The following examples will further illustrate this invention but the invention is not restricted to these examples. The parts are by weight.

**Example 1**

Sodium sulfate of technical purity has 5 per cent of sodium oxalate added thereto and is then treated in a rotary tubular furnace with hydrogen at a temperature of 650° to 700° C. After treatment for 3 to 4 hours, a 95 to 99 per cent sodium sulfide of pale color is obtained.

**Example 2**

970 parts of commercial sodium sulfate are intimately mixed with 30 parts of sodium tartrate and treated for 6 hours at 680° C. with hydrogen. A high percentage sodium sulfide is obtained.
Example 3

Sodium formate is added to a solution of sodium sulfate in such an amount that in the salt obtained by evaporating the solution to dryness there are 50 parts of sodium formate to 950 parts of sodium sulfate. By reducing this salt under the conditions employed in Example 1 or 2, a colorless or pale rose-colored granulate is obtained which contains at least 95 per cent of sodium sulfide.

What we claim is:

1. A process for the production of sodium sulfide by the reaction of sodium sulfate with reducing gases at temperatures of 600° to 800° C. which comprises subjecting to the action of said gases a sodium sulfate which contains a subordinate amount of the sodium salt of lower aliphatic carboxylic acid having up to two carboxyl groups.

2. A process for the production of sodium sulfide by the reaction of sodium sulfate with reducing gases at temperatures of 600° to 800° C. which comprises subjecting to the action of said gases a sodium sulfate which contains a subordinate amount of sodium formate.

3. A process for the production of sodium sulfide by the reaction of sodium sulfate with reducing gases at temperatures of 600° to 800° C. which comprises subjecting to the action of said gases a sodium sulfate which contains a subordinate amount of sodium acetate.

4. A process for the production of sodium sulfide by the reaction of sodium sulfate with reducing gases at temperatures of 600° to 800° C. which comprises subjecting to the action of said gases a sodium sulfate which contains a subordinate amount of sodium carboxylic acid having two carboxyl groups.

5. A process for the production of sodium sulfide by the reaction of sodium sulfate with reducing gases at temperatures of 600° to 800° C. which comprises subjecting to the action of said gases a sodium sulfate which contains a subordinate amount of sodium oxalate.

6. A process for the production of sodium sulfide by the reaction of sodium sulfate with reducing gases at temperatures of 600° to 800° C. which comprises subjecting to the action of said gases a sodium sulfate which contains a subordinate amount of sodium tartrate.

7. In a process for the production of sodium sulfide by reducing solid sodium sulfate with a reducing gas at a temperature below the fusion temperature of the reaction mixture, the improvement which comprises incorporating in the reaction mixture a sodium salt of a lower aliphatic carboxylic acid having up to two carboxyl groups in a minor amount sufficient to accelerate the said reduction.

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