METHOD FOR OXIDIZING POTASSIUM FERROCYANIDE TO POTASSIUM FERRICYANIDE

Fig. 1.

Fig. 2.
METHOD FOR OXIDIZING POTASSIUM FERROCYANIDE TO POTASSIUM FERRICYANIDE

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This invention relates to the purification of gases by oxidation of hydrogen sulphide with ferrocyanide of potassium and reconstitution of the ferrocyanide of potassium formed to reconstitute ferrocyanide of potassium.

In practice the purification of gases by oxidation of hydrogen sulphide with potassium ferrocyanide could not be carried on on a large industrial scale on account of important economical difficulties arising, particularly with regard to the necessary reconstitution.

For example, when this reconstitution was effected with air under pressure, the drawback was experienced that an important part of the complex cyanogen salts was lost. Such loss is avoided with electrolytic reconstitution, but until now electrolysis could only be carried out in electrolytic cells provided with diaphragms, so that in practice the method of electrolytic reconstitution could only be regarded as too expensive to permit of economic working. Experimental attempts to produce ferrocyanide of potassium electrolytically in a cell devoid of a diaphragm have shown that the reconstitution of ferrocyanide of potassium is even less economical than in the case where cells with diaphragms were employed.

According to the present invention the problem of reconstituting the ferrocyanide electrolytically is solved in a manner which permits the use, instead of the expensive special electrodes, for instance of nickel or the like, of technically and economically cheap electrodes of iron or at least of conductors consisting mainly of iron.

As the result of experimental research it is found that when a solution of ferrocyanide of potassium is electrolyzed in known manner with or without previous addition of caustic alkali or alkali carbonate in an electrolytic cell with or without a diaphragm, and for instance with electrodes of iron, with continuous electrolysis one electrode is covered with a blue layer of a thickness which continuously increases, which, however results in a terminal voltage of excessively high degree, while the current density remains the same. The iron is strongly corroded anodically, and therefore cannot be used.

I have found that this corrosion of the electrodes can in practice be completely avoided if the caustic potash present in the solution is converted into potassium carbonate.

This conversion may be effected by adding bi-carbonate or potassium to the electrolyte, or added potassium carbonate may be converted into bi-carbonate by adding carbonic acid before the commencement of the electrolysis or while the electrolysis is in progress. The carbonic acid or the bi-carbonate thus converts the caustic potash present or produced into potassium carbonate. It has also been observed that, when operating in this manner, a diaphragm is unnecessary, since reduction of the cyanide of potassium anodically formed does not take place at the cathode to any extent worth speaking of, the less so if it is not necessary to convert the ferro-cyanide of potassium completely into ferricyanide of potassium.

In fact further experiment and research were required before it was practicable to combine the process of electrolytic reconstitution with the oxidation of hydrogen sulphide from gases. Thus, if alkaline cyanogen lyes are used for absorption and oxidation of the hydrogen sulphide present in gases care must be taken that there is always ferrocyanide of potassium present in the electrolyte at least to a small extent. If the oxidizing ferrocyanide of potassium is completely used up, further combination of the hydrogen sulphide and the formation of potassium sulphide would take place in the balance with the rest of the salt of the electrolyte, which again would result in prejudicing the economy with continuous electrolysis when using, by way of example, iron electrodes and a cell without a diaphragm owing to the considerable increase of the terminal voltage in the cell by formation of a protective blue layer containing sulphur on the anode. If, however, ferrocyanide of potassium containing little ferricyanide of potassium is subjected to electrolysis, there is the possibility of working with a sufficiently high load of current at the...
electrode faces and with a terminal voltage of about 1.6 to 2.2 volts per cell, since sulphide of potassium is not present in the electrolyte.

5 The amount of ferricyanide of potassium need not be more than very slight. If the process is to be conducted cyclically and the hydrogen sulphide to be oxidized by the ferricyanide of potassium is only present in the gases in a comparatively low degree of concentration, it is of advantage to use a large amount of wash liquor in the cycle.

Since in this case, moreover, ferricyanide of potassium is produced at an intermediate stage, it is of advantage to effect only a slight conversion of the ferricyanide of potassium present in the electrolyte into ferricyanide of potassium in order to maintain a terminal voltage as low as possible.

20 By the invention the economic separation of the sulphur from the liquor is rendered possible. In washing the gases with a solution of ferricyanide of potassium the sulphur will remain in the liquor in a state of a very fine colloidal suspension. It is only theoretically possible but practically impossible to separate such sulphur by filtration, inasmuch as the colloidal sulphur clogs the filter pores. Complete separation of the sulphur by settling would render the process too expensive.

If now electrolytic cells are used without diaphragms, the revivification of the ferricyanide to constitute ferricyanide of potassium will not be impaired by the fact that the electrolyte contains sulphur. On this observation depends a further feature of the invention according to which a continuous cycle is established without filtration of the sulphur in that from the circulating liquor only that amount of sulphur is continuously removed which is converted from the colloidal state into a state in which it is adapted to settle, because, though the sulphur passing into the liquor on the oxidation of the hydrogen sulphide is present at first in a state of fine suspension and more or less in a colloidal state, it is in part changed into a state in which it is adapted to settle on an increasing enrichment of the liquor with sulphur. Only this latter part is removed continuously.

By way of example, the process can be carried out in this way, that after washing the gases with a solution of ferricyanide of potassium, the liquor containing sulphur is passed through settling vessels of large dimensions before it is allowed to enter the electrolytic cells devoid of diaphragms. In these vessels that part of the sulphur is separated which has changed from the colloidal state into a coarser state and is adapted to settle by gravity. The rest of the sulphur, which is still in a state of fine suspension, will pass through the electrolytic cells together with the liquor without affecting the electrolysis. The particles of sulphur that have passed through the electrolytic cells will in the next stage of the cycle be separated out wholly or in part in the settling vessels if present in the liquor to a sufficient extent to consolidate into coarser particles.

In the performance of the cyclic process in which from the circulating liquor only the amount of sulphur changed from the colloidal state into the state in which it can settle by gravity can be continuously removed there is the difficulty of providing a suitable electrolytic device which is adapted to handle the extraordinarily large amount of the liquor to be electrolyzed, and to allow the passage of the liquor in such manner that no undesired settling of the sulphur will take place therein.

To permit the operation to be carried out with the minimum current density it is necessary that, apart from the conditions mentioned above, as large as possible electrode surfaces should be provided with the minimum amount of cast material. These conditions as well as other requirements for reliable and convenient operation are fulfilled according to the invention, which contemplates the use of electrolytic cells adapted to allow the liquor to run through, which cells are formed by cast iron plates which are assembled by-polarly to constitute a battery, and which for the sake of increasing the surface are provided with ribs or the like mating with one another and using as little cast material as possible. The ribbed plates are provided at the edges with jointing flanges or the like, a pair of adjoining plates forming a cell.

The mounting or assembling of the plates is very simple, the rows of ribs of adjoining plates mating with one another thus forming a very active electrode surface. The expression "ribs" is not intended to be limited to ledge-like projections, but all kinds of projections, no matter of what shape, are to be understood hereby. The plates are preferably reduced at the inlet and outlet ends and the ribs are extended only in part into the reduced ends.

In the accompanying drawing apparatus according to the invention is illustrated by way of example.

Fig. 1 is an elevation of an upright plate, and
Fig. 2 a section of parts of two plates drawn to a larger scale.

As may be gathered from Fig. 2, the plate 1 is provided on both sides with ribs 2 which are staggered in such manner that the ribs on both sides of the plate project into the spaces intermediate the ribs of the adjoining plates. One side of the plate 1 is provided with a peripheral flange 3 of about the same height as the ribs and abutting against a peripheral bearing face 4 of the next adjoining plate, a packing strip or ring 5 being interposed. Each end 6 of each plate is reduced...
in breadth towards the inlet 7 or the outlet 8 for the liquor. From Fig. 1 it will be seen that the ribs 2 project only partly into the reduced ends 6.

The liquor to be revivified enters from below at the contracted end and is distributed while rising upwardly in the channels between the ribs of the plates. After being saturated with bubbles of hydrogen and oxidized the liquor emerges through the contracted outlet at the upper end of the cell. The arrangement of a conical inlet and outlet at the ends of the cell permits even distribution of the liquor in continuous circulation—which is necessary for reliable and uniform revivification of the liquor. Since no horizontal faces are presented, there will be no settling of the sulphur in the apparatus.

I claim:

1. A method of electrolytic revivification of ferrocyanide of potassium formed in the purification of gases by oxidation of the hydrogen sulphide by ferricyanide of potassium, characterized in that the anodic oxidation of a solution of ferrocyanide of potassium containing at least a small quantity of ferricyanide of potassium is effected in an electrolytic cell or cells without a diaphragm and that the caustic potash formed in the electrolysis in the nascent state is converted into alkali carbonate by alkali bi-carbonate.

2. The method according to claim 1, further characterized in that an electrode consisting mainly of iron is used.

3. The method according to claim 1 further characterized in that the purification is effected in a continuous cycle without filtration of the sulphur, there being continuously removed from the liquor that amount of sulphur which passes from the colloidal state into a state capable of settling.

In testimony whereof I have signed my name to this specification.

RICHARD BRANDT.