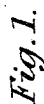
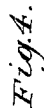


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No. 579,639.

Patented Mar. 30, 1897.



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PROCESS OF AND APPARATUS FOR MAKING CYANIDS.

SPECIFICATION forming part of Letters Patent No. 579,639, dated March 30, 1897.

Application filed February 17, 1896. Serial No. 579,644. (No model.) Patented in England April 26, 1894, No. 8,305.

To all whom it may concern:

Be it known that we, HORACE WOODWARD CROWTHER, residing at The Beeches, West Bromwich, EDMUND CHARLES ROSSITER, residing at Smethwick, both in the county of Stafford, JOHN JAMES HOOD, residing at 1 Fenchurch Avenue, in the city of London, all chemists, and GEORGE STACEY ALBRIGHT, gentleman, residing at The Elms, Edgbaston, Birmingham, in the county of Warwick, England, have invented certain new and useful improvements in the manufacture of ferrocyanids and cyanids of potassium and sodium from their sulfocyanids, and apparatus relating thereto, (for which we have received Letters Patent in Great Britain, No. 8,305, dated April 26, 1894,) of which the following is a specification.

It is well known that sulfocyanids of the alkalis may be converted into their ferrocyanids by heating with metallic iron and subsequently lixiviating the product with water. It is very important, as has been pointed out before, that the sulfocyanids should be quite free from water, and also that the iron used should be clean and free from oxid. Partly owing to these conditions being difficult to satisfy and partly owing to unsatisfactory apparatus having been employed the reaction has not been brought into general use for manufacturing purposes.

The sulfocyanid of potassium is difficult to dry by heat alone, as the last portions of the water are obstinately retained. We find the best method of drying is to force through the mass melted by heat an inert gas, such as nitrogen or carbonic-acid gas or limekiln-gases, which latter we prefer to use, as they are easily obtainable. The limekiln-gases should contain as little oxygen as possible. The temperature of the sulfocyanid of potassium is gradually raised until about 450° to 500° Fahrenheit is reached. The inert gas, besides driving out the water, protects the sulfocyanid from oxidation or firing as the temperature rises. As the melting-point of the damp crystals and the fusion-point of the dry sulfocyanid of potassium are very near together no mechanical agitation is necessary.

In the case of sulfocyanid of sodium, which crystallizes with two molecules of water, the salt first melts in its water of crystallization,

and as this is driven off the anhydrous salt settles on the bottom of the pot and thus renders further drying difficult. We prefer to dry this salt with the aid of mechanical agitation, which will be described more fully below, whereby at first a dry anhydrous sulfocyanid of sodium, as a loose powder, is obtained, which when the temperature is raised fuses. To prevent firing or oxidation of the sulfocyanid, we pass into the pot inert gas, such as limekiln-gases, but in this case the gases need not necessarily pass through (and we prefer them only to pass over) the sulfo-

Our method of preparing iron free from oxid is to treat such iron with a soluble sulfid. The mother-liquors after the separation of the ferrocyanid of potassium or ferrocyanid of sodium obtained in the manufacture of ferrocyanid by this method are well suited for the purpose. After such treatment the iron is washed with water to remove any soluble sulfid, well drained, and then as speedily as possible without further drying put into the just-melted mass of sulfocyanid of potassium or sodium. This is done just after the first melting and before any appreciable amount of water has been driven off. The sulfocyanid and the iron are then dried together, as described above. If iron borings are obtainable free from any appreciable quantities of rust or oxid, we simply dry the iron at a gentle heat and add it to the fused sulfocyanid of potassium or sodium after the drying operation has been completed.

When the conversion of the sulfocyanid into cyanid is intended, it is equally important that the sulfocyanid should be in a dry state, and the means above described for drying it are especially suitable.

The apparatus we prefer to employ is shown by the drawings annexed.

Figure 1 is a plan, partly in section. Fig. 2 is a vertical section through line E F. Fig. 3 is a front elevation. Fig. 4 is a detail view of the cover of one of the pots. Fig. 5 is a detail view of the blowpipe employed. Fig. 6 is a detail view of the perforated portion of the blowpipe.

Fig. 1 shows a convenient arrangement of four furnaces—viz., two furnaces with no mechanical apparatus overhead for stirring,

which may be used for drying the potassium-sulfoeyanid, and two furnaces with the overhead mechanical apparatus for agitation required for the fusion together of the dried sulfoeyanid and iron. The drying and decomposing furnaces are alike. The furnaces are preferably cylindrical, lined with fire-brick, and built in the manner shown in the drawings. The top of each is covered with an iron plate having a hole in the center somewhat larger than the outside diameter of the pot. Near the top are a number of lateral openings *b*, which connect to the flue *c* and thence to the chimney. The heated gases from the fire underneath the pot pass up all round the pot, whereby it is heated uniformly. The flames or hot gases pass through the openings *b* into the annular flue *c* and thence to a chimney. Dampers are provided to regulate the draft.

The mechanical arrangements for agitating the mixture of sulfoeyanid and metal are a main shaft *d*, driven by an engine, which by means of the pulleys and belts, as shown, communicates its motion to beveled wheels *e'* and *f'* and thence to the vertical shaft *f*, which is so arranged as to be exactly over the center of the pot when the pot is in position in the furnace. The shaft *f* is so arranged at its lower end that it may be coupled with the removable piece *g* and then to the stirrer or agitator in the pot beneath. The removal of this piece *g* allows of the introduction or withdrawal of the pot from the furnace. The stirrer *h* consists of an axis, square at its lower part and having strong iron arms or paddles bolted on, as shown. The stirrer is supported in the pot by the collar *h'* on the agitator-axis resting upon the cross-bar *i*, which is supported some little distance above the top of the pot by the pillars *p p*, fastened on the top flange of the pot, the top cross-bar *i* serving to keep the shaft vertical and to add rigidity to the stirring apparatus. The cross-bars are so fixed on the pillars that they are removable with the agitator.

The pot we prefer to use is cylindrical. The top flange, besides serving for supporting the pillars for carrying the cross-bars mentioned above, also serves for fastening the cover onto the pot. It has also a lower flange *x* to support the pot in the furnace at a proper height above the fire. This flange is of sufficient width so that it rests firmly on the iron plate covering the top of the furnace, as mentioned above. The pot is also furnished with lugs *k k* to receive hooks attached to crane-chains to enable the pot either to be removed from the drying-furnace to the decomposing-furnace or from this to a place to cool. An overhead traveling crane (not shown in the drawings) is convenient for the purpose. The pot is also furnished with a movable cover *j*, Fig. 4, made in two halves and nearly air-tight. It is fastened onto the pot by means of bolts, with a joint of asbestos packing between it and the pot. A small

sight-hole is provided in the lid, which is closed by a plug when not in use.

The drying of the sulfoeyanid and the fusion of the sulfoeyanid with the metal are done in the same pot; but in the case of sulfoeyanid of potassium the first operation of drying takes place in the drying-furnace and the decomposition in the decomposing-furnace.

We proceed to perform the operations as follows: For the conversion of sulfoeyanid of potassium into ferrocyanid a known quantity of the sulfoeyanid is put into the pot, which when melted will occupy about one-third the capacity of the pot. The pot is then put into the drying-furnace, and the sulfoeyanid is just melted by the fire underneath. Then the iron (if found necessary to treat in the manner above described) is added and the two are dried together by further heating, while inert gases (limekiln-gases) are passed through by means of a pipe *x*, having a ring *y* at the bottom perforated with a number of small holes, Fig. 5. This pipe is connected by means of a stout india-rubber tube or pipe to a main supplying the inert gas (limekiln-gases) under pressure and free from water. When the temperature reaches 450° to 500° Fahrenheit and the fused sulfoeyanid is free from water, the gas-pipe is removed and the pot transferred to the decomposing-furnace. The agitator is introduced and connected by means of the piece *g* to the vertical shaft *f*. The lids having been fastened on, the pot is fired, the materials being continually stirred. When the reaction has taken place, the mass inside becomes red-hot and is then stirred only with difficulty. The connecting-piece is then disconnected from the agitator and shaft, and the pot (together with agitator) is taken from the furnace to a place to cool.

If the iron is practically free from oxid, and therefore requiring no treatment, as described, the sulfoeyanid is dried by itself, and the iron previously dried is added after the pot has been removed to the fusion or decomposing furnace, the agitator running at the same time. The subsequent procedure is as described above.

In the case of sulfoeyanid of sodium the pot, with the agitator fitted and containing a charge of sulfoeyanid of sodium, is at once put into the decomposing-furnace and the sulfoeyanid melted in its water of crystallization and the treated iron added, (if found necessary to treat the iron.) The charge is dried by heat and continuous stirring until a greater part of the water has been removed. Then a stream of inert gas (limekiln-gases) is passed into the pot to prevent oxidation of the iron and sulfoeyanid. The heat is then raised with continual stirring and passage of limekiln-gases over the surface until the mass is fused. The lid is then fastened on. The subsequent procedure is then exactly the same as described in the case of the potash-salt.

If it is not necessary to treat the iron as

above described, the sulfocyanid is first dried and fused in the manner described, the dried iron being added after the sulfocyanid is in a state of fusion.

5 To facilitate the removal of the charge from the pots, it is as well to pull up the agitator so that the top paddle touches underneath the cover. This breaks up the mass in the pot and enables it when cold to be easily removed.

10 We use sixty-five parts or thereabout of iron to every ninety-seven parts sulfocyanid of potassium or eighty-one parts sulfocyanid of sodium. The iron we prefer to use is fine turnings or borings.

15 When the pots have become cold, the lids and agitators are removed and the mass transferred as speedily as possible to a vat, a suitable quantity of water being added. The contents of the vat are boiled by live steam until the mass is disintegrated and the whole of the cyanid converted into ferrocyanid. The steam is then stopped, the sulfid of iron allowed to settle, and the clear liquor is removed by decantation and evaporated to a suitable strength for crystallization. We prefer to boil down to such a strength that only a very small quantity of prussiate remains in the mother-liquor. The sulfid of iron left in the vat is filtered and washed free or nearly free from ferrocyanid. The weak liquors are used again for dissolving fresh charges. The crude prussiate is then freed from as much mother-liquor as possible and then by recrystallization, as is well understood, made into pure or nearly pure ferrocyanid of potassium or sodium of commerce.

20 The mother-liquors left from the first crystallization of the ferrocyanid contain sulfid of potassium or sodium with any undecomposed sulfocyanid. The sulfids are converted into carbonates by the action of carbonic acid, and the carbonates so formed are used for precipitating fresh quantities of the sulfocyanid of calcium liquor, from which we thus in the first instance obtain sulfocyanids of K and Na.

25 When it is desired to produce cyanid of potassium, sulfocyanid of potassium is dried in all respects as already described, and the pot having been transferred to the decomposing-furnace the agitator is introduced and connected by means of the piece *g* to the vertical shaft *f*. The necessary amount of zinc or lead or other metal that does not form a sulfid soluble in solution of alkaline cyanid in a suitable state of division or in the molten state is then added, or preferably a portion is added and the remainder at a later period.

30 The lids having been fastened on, the pot is fired, the materials being continually stirred. As the reaction takes place the mass inside becomes red-hot, and samples are from time to time withdrawn to find when the decomposition of the sulfocyanid is sufficiently complete. When this is found, the connecting-piece is disconnected from the agitator and

shaft, and the pot, together with the agitator, is taken from the furnace to cool.

35 In the case of sulfocyanid of sodium the pot, with the agitator fitted and containing a charge of sulfocyanid of sodium, is at once put into the decomposing-furnace and the sulfocyanid melted in its water of crystallization. The charge is dried by heat and continuous stirring until a greater part of the water has been removed. Then a stream of inert gas (limekiln-gases) is passed into the pot to prevent oxidation of the sulfocyanid. The heat is then raised, with continual stirring and passage of limekiln-gases over the surface, until the mass is fused. The lid is then fastened on and the necessary quantity of zinc, lead, or other suitable metal is added. The subsequent procedure is then exactly the same as described in the case of the potash-salt.

40 The mixture of cyanid of the alkali and sulfid of zinc, lead, or other metal used is then lixiviated with water, the insoluble sulfid separated by filtration, the solution evaporated *in vacuo*, and the resulting solid alkaline cyanid dried, if necessary, *in vacuo* and fused.

45 What we claim is—

1. The herein-described method of preparing the iron used in the manufacture of ferrocyanid of potassium or sodium from their sulfocyanids, which consists in treating it with an alkaline sulfid or sulfid of an alkaline earth.

2. The herein-described method which consists in treating iron with an alkaline sulfid or sulfid of an alkaline earth, mixing it with a sulfocyanid, and then drying the mixture in the presence of an inert gas.

3. The herein-described apparatus comprising a furnace, a pot arranged over the furnace and removable therefrom, an agitator, a power-driven shaft *f*, a detachable coupling *g* between the shaft and the agitator, the pillars *p* connected with a flange on the pot, cross-pieces connecting the pillars and supporting the agitator-shaft, and a cover made in sections having an air-tight connection with the pot.

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