

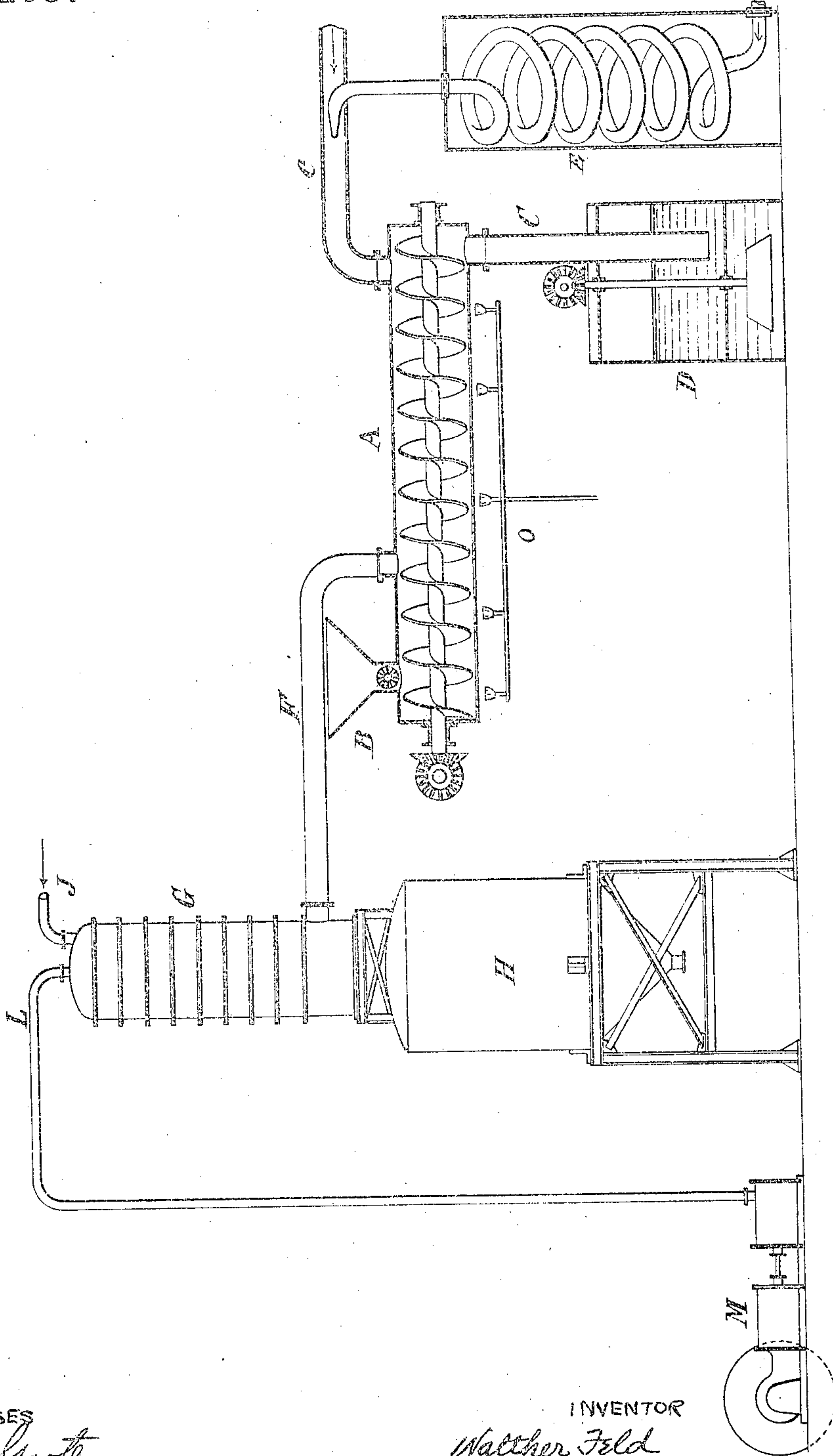
W. FELD.

PROCESS OF RECOVERING HYDROCYANIC ACID.

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922,409.

Patented May 18, 1909.



WITNESSES

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PROCESS OF RECOVERING HYDROCYANIC ACID.

No. 922,409.

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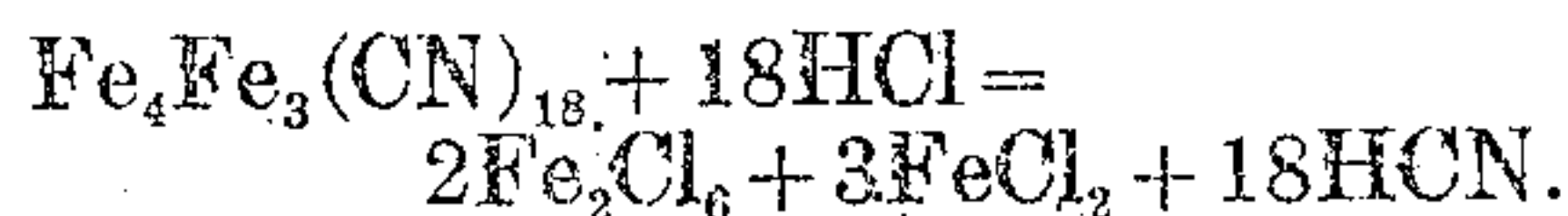
To all whom it may concern:

Be it known that I, WALTHER FELD, a subject of the King of Prussia and the German Emperor, of Hönningen-on-the-Rhine, in the German Empire, have invented new and useful Improvements in Processes of Recovering Hydrocyanic Acid, of which the following is a specification.

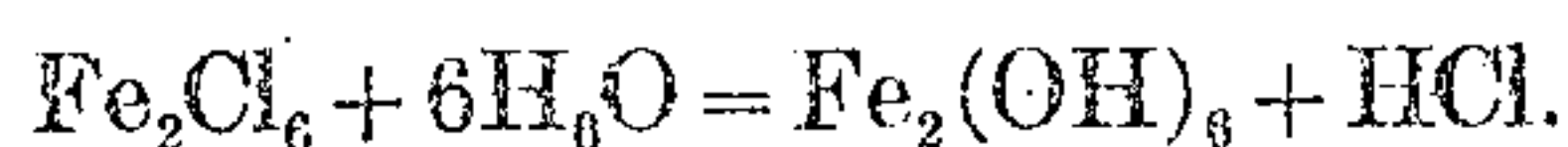
In order to obtain hydrocyanic acid from metallic cyanids, such as iron cyanids and others, they have been distilled with acids, but, by this process the yield of hydrocyanic acid is small and in addition to hydrocyanic acid, products of decomposition and condensation are formed, and part of the metallic cyanid remains undecomposed. Hydrocyanic acid has also been obtained by heating solutions of cyanids with salt solutions, but this process is applicable only to the treatment of alkali or earth alkali cyanids, and not to iron cyanids and the like.

According to my invention, metallic cyanids, such as iron cyanids (alkali or earth alkali or other ferrocyanids, ferricyanids, Prussian blue, and the like) are completely decomposed so as to yield only hydrocyanic acid by treating them while hot, in a solid or damp state (but not in the form of a solution) with steam together with an acid in such manner that while the reaction proceeds, the reacting mass is not covered by the liquid, or liquids. Such acid may be added in form of liquors or vapors periodically or continuously to the cyanid to be distilled. Instead of acids I may use acid salts, or such salts as will when heated in a solid or moist state with steam, yield acid by decomposition. Suitable acids for the purposes of my invention are hydrochloric, hydrobromic, nitric, sulfuric, phosphoric and silicic acid, and suitable salts are all the acid salts of the above mentioned acids and their neutral or basic salts with ammonia, magnesia, alumina, manganese, zinc, iron, copper, or lead. The use of such salts, instead of acids, has the advantage that in the course of the reaction no free acid is formed, which, if formed

would contaminate the hydrocyanic acid. The reaction is complete if even less salt is used than is equivalent to the cyanid to be decomposed. If, for example, ammonium chlorid in the presence of steam act upon heated Prussian blue, iron chlorid is formed and a mixture of hydrocyanic acid is distilled. The reaction may be expressed as follows:



The iron chlorid, under the influence of steam, yields iron hydroxid and hydrochloric acid, this acting upon undecomposed cyanid. This reaction may be expressed as follows:



The same reaction takes place if other of the above mentioned salts be used.

In order to prevent acid vapors being mixed with the hydrocyanic acid at the end of the reaction, the vapors of the acid of the reaction are absorbed by basic compounds of the salts employed. This may be accomplished in any suitable manner, as for instance by adding such basic compounds of the salts (hydrates or carbonates of magnesia, iron oxid and the like) to the reacting mixture. These basic substances if heated, will absorb only the vapors of the reaction acids and not hydrocyanic acid. The use of such basic compounds with the reacting mixture will not interfere with the completeness of the reaction, even if less acid; or less basic, neutral, or acid, salt be used than is equivalent to the metallic cyanid to be decomposed. Part of the acid acts upon the basic compound and forms the corresponding salt, which then acts upon the cyanid as hereinbefore described with regard to ammonium chlorid. If the acid be well mixed with the metallic cyanid, the contamination of the hydrocyanic acid by the vapors of the reaction acid will be avoided, even if no basic compound be added as above described to ab-

sorb the same. In this case also it is possible to complete the reaction with less acid than is equivalent to the metallic cyanid.

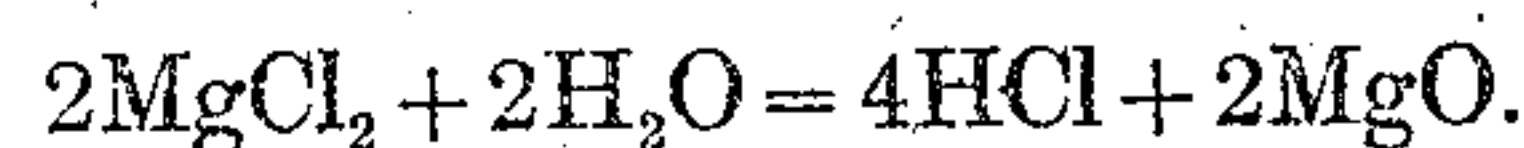
The steam may be used either saturated or superheated, and of either high or low pressure, or in partial vacuum. Instead of steam, saturated or superheated gases containing steam may be used. The reacting mixture (containing the metallic cyanid and acid or acid-yielding compound) may be heated by heating the reaction vessel or by passing a heated gas through the reacting mixture or both.

If the reaction vessel be heated sufficiently to vaporize water, the necessary steam for the process may be obtained by merely adding water to the reacting mixture. This water may conveniently carry the acids or salts in solution. But if water be used in this manner, the amount employed and the degree of heat must be so regulated that the reacting mixture is never covered by liquid, but merely moistened, and that the water is vaporized the moment it comes in contact with the walls of the reaction vessel. Instead of either water or steam, a compound may be used which will yield steam when heated. Basic salts or neutral hydrates of metals are suitable for this purpose. Care must be taken that the chamber in which the reaction takes place is always filled with steam, which, in addition to reacting as described, will act as a carrier for the hydrocyanic acid formed by the reaction. Such carrying medium is necessary in order to avoid local saturation of hydrocyanic acid vapors in the reacting mass, which might interfere with the completion of the reaction.

From the foregoing description the method of working for each case will be readily understood. The particular method of working, the temperature of decomposition (which in any case must be above 100° centigrade), and the arrangement of the apparatus, must depend on the nature of the metallic cyanid to be decomposed, the distillation agent (acid, acid salt, or acid-yielding salt,) used, and the purpose for which the hydrocyanic acid obtained is to be used. The said hydrocyanic acid may be used for any process. It may be absorbed by hydrates or carbonates of alkalies or earth alkalies in a solid or liquid form, or it may be used for the obtainment of ferrocyanids or ferricyanids or of organic nitrogen compounds of any composition.

The following is an example of how the process according to this invention may be performed in the treatment of Prussian blue with chlorid of magnesium, but I do not limit myself to these compounds, nor to the proportions and temperatures hereafter given, as they may be varied according to

each particular case. The parts are by weight. The Prussian blue is presumed to be in a damp state, containing about 50 per cent. of solid $\text{Fe}_4\text{Fe}_3\text{Cy}_{18}$. One hundred parts of the Prussian blue are mixed with a quantity of magnesium chlorid, (in solid crystals, or in a fused condition, or in concentrated solution) equivalent to about twenty parts of MgCl_2 . A greater, or smaller, amount does not influence the completeness of the reaction, but has only an accelerating, or retarding, influence. This reaction may be expressed as follows:



The reaction of the hydrochloric acid with the Prussian blue is the same as above indicated. To obtain the hydrocyanic acid free of hydrochloric acid, five parts of magnesia may be added. By mixing, the agents become liquid, but no hydrocyanic acid is formed, even if the mixture be warm.

Any suitable apparatus may be used for the distillation of the mixture which will allow the said mixture to be gradually charged, heated and tested. For example, a revolving apparatus which will allow continuous working, such as is shown in the accompanying drawing may be used.

A horizontal apparatus A with a revolving worm inside, is here shown. The apparatus may be kept under a slight vacuum by the exhaust M in order to avoid danger by escape of hydrocyanic acid at parts of the apparatus which may not be sufficiently tight. The reacting mixture is continuously charged at B into one end of this apparatus; and, at the opposite end, steam and a current of gas, for example carbonic acid gas enter through the pipe e. This mixture of gas and steam is preferably superheated at E to from 250° to 350° centigrade. If superheated steam be used, the reaction is quicker and less steam is required and therefore the hydrocyanic acid obtained will be less diluted. The addition of gas accelerates the carrying off of the hydrocyanic acid. The steam and the reacting mixture travel in opposite directions. External heat may be applied to the reaction chamber by any suitable means for instance by a series of Bunsen burners O. The farther the reacting mixture advances in the apparatus, the more it is heated and gives off water vapors till the mixture has advanced to that part of the apparatus where hydrocyanic acid is distilled at a temperature between 150° and 350° centigrade. The speed at which the mixture passes through the apparatus and the heating are so regulated that the reaction is complete before, or when the mixture arrives at the end where steam and gas enter. At this end of the apparatus a discharge pipe C leads the exhausted material into a receptacle D con-

taining water, or a solution of magnesium chlorid. The material, by falling into this liquid, is cooled to such a degree that no further reaction takes place, and in case any undecomposed cyanid should accidentally have remained in the mass, danger to the operators is avoided. The liquid extracts from the solid mass any magnesium chlorid remaining undecomposed which is thus regenerated. The insoluble iron oxid is separated from the liquid by filtration, or decantation, and can be used for the extraction of cyanogen from coal gases and the like. If the process be carried on as hereinbefore described, most of the magnesium chlorid will be regenerated so that the reaction will be effected at the cost only of the steam.

The gas and steam carrying the hydrocyanic acid leave the reaction chamber through the pipe F and enter the absorption apparatus G. This comprises a series of superposed chambers filled with caustic soda which enters by the pipe j. The gases are washed by this and the hydrocyanic acid and steam are absorbed, the waste gases passing off to the exhaust M through the pipe L. The cyanid of soda solution is collected in the vessel H.

The process may be used for the decomposition of any metallic cyanid, also for double cyanids for instance, for ferro- and ferricyanids of alkalies, earth alkalies, ammonia, iron and other metals and bases.

In the following claims it is to be understood that the mention of the metallic cyanids being in a "solid condition" includes a moist condition other than a solution; that "steam" means either steam as such (superheated, or not,) or steam contained in a gas, or gases, or steam derived from a compound yielding steam when heated with the acid, or salt, and that acid means acid liquor or vapors and that "salt" means a basic, neutral or acid salt which, when heated with steam, will yield an acid, or acid vapor.

I claim:—

1. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of steam to the action of acid and maintaining the reacting mass at least in part above the reaction liquid.

2. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of steam to the action of a salt yielding acid during the reaction and maintaining the reacting mass at least in part above the reaction liquid.

3. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence

of steam to the action of acid and maintaining the reacting mass at least in part above the reaction liquid, absorbing the acid vapors without affecting the hydrocyanic acid.

4. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of steam to the action of a salt yielding acid during the reaction and maintaining the reacting mass at least in part above the reaction liquid, and absorbing the acid vapors by basic compounds of said salts.

5. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of steam to the action of acid less in proportion than is equivalent to the metallic cyanid and maintaining the reacting mass at least in part above the reaction liquid.

6. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of steam to the action of acid intimately mixed with said cyanid and maintaining the reacting mass at least in part above the reaction liquid.

7. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . to the action of acid and a substance yielding steam under heat and maintaining the reacting mass at least in part above the reaction liquid.

8. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of steam to the action of acid and maintaining the reacting mass at least in part above the reaction liquid.

9. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of steam and gas to the action of acid and maintaining the reacting mass at least in part above the reaction liquid.

10. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of superheated steam to the action of acid and maintaining the reacting mass at least in part above the reaction liquid.

11. The process of obtaining hydrocyanic acid from metallic cyanids in a solid state which consists in subjecting the latter at a temperature above 100°C . and in the presence of superheated steam and a gas to the action of acid and maintaining the reacting mass at least in part above the reaction liquid.

12. The process of obtaining hydrocyanic

acid from metallic cyanids in a solid state
which consists in subjecting the latter in a
reaction vessel to the action of acid in the
presence of steam, externally heating said
5 vessel during the reaction and maintaining
the reacting mass at least in part above the
reaction liquid at a temperature above 100°C.

In testimony whereof I have signed my
name to this specification in the presence of
two subscribing witnesses.

WALTHER FELD.

Witnesses:

WOLDEMAR HAUPT,
HENRY HASPER.