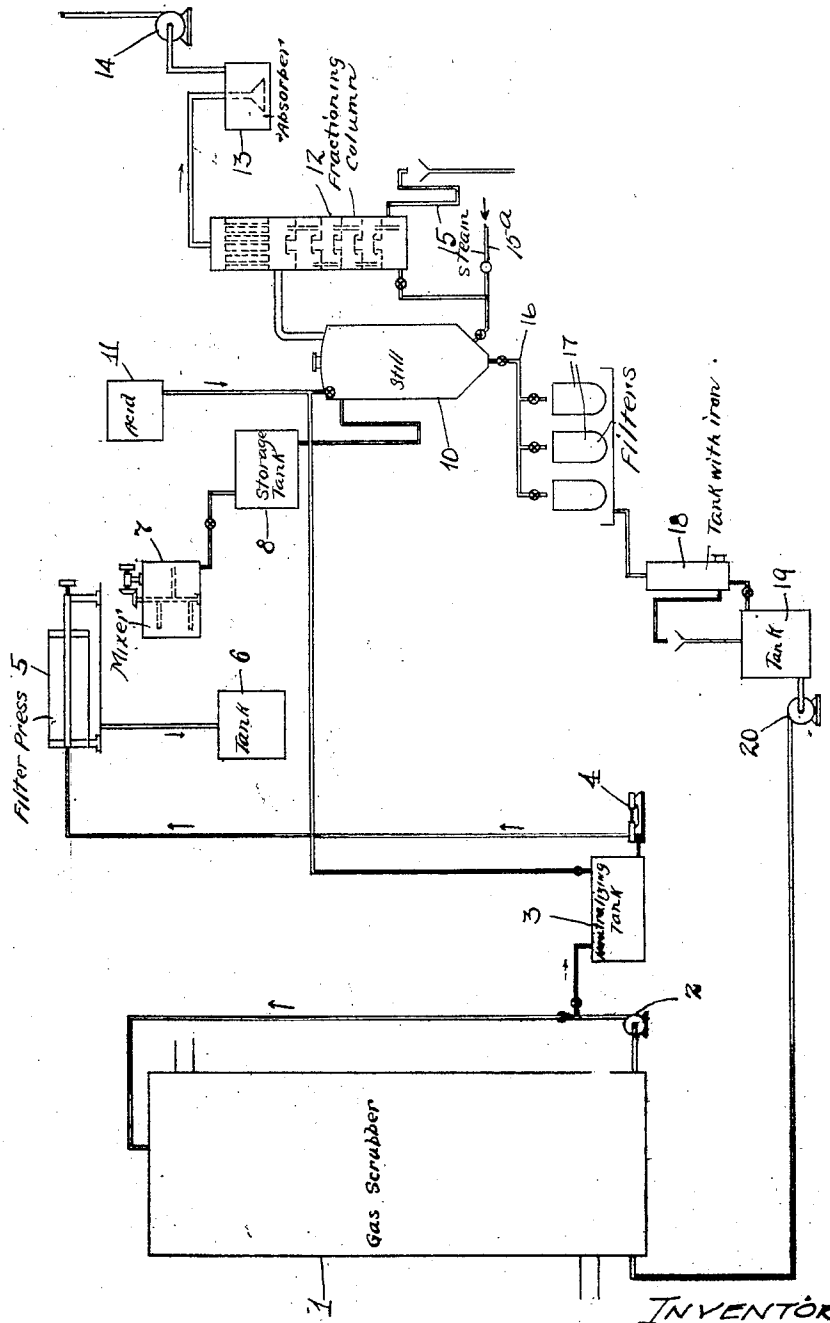
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METHOD OF MAKING HYDROCYANIC ACID AND CYANIDS.

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1,347,518. **Patented July 27, 1920.**



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To all whom it may concern:

Be it known that I, MAX E. MUELLER, a citizen of the United States, and a resident of Youngstown, county of Mahoning, and State of Ohio, have invented a new and useful Improvement in Methods of Making Hydrocyanic Acid and Cyanids, of which the following is a specification, the principle of the invention being herein explained and the best mode in which I have contemplated applying that principle, so as to distinguish it from other inventions.

It has been recognized that to obtain cyanid from ferrocyanid in the wet way by distilling such ferrocyanid with an acid, and absorbing the evolved hydrocyanic acid in a caustic alkaline solution, involves unexpected and peculiar difficulties. One of these (see H. E. Williams' "*Cyanogen Compounds*," p. 272, *et seq.*) is the difficulty that when an alkali metal ferrocyanid is distilled with a dilute mineral acid, only fifty per cent. of the total cyanogen is evolved as hydrocyanic acid, the remainder being precipitated as the insoluble ferrous potassic (or sodic, etc.) ferrocyanid. Moreover, in some methods of extracting cyanids from gases the cyanogen is combined in a compound similar to the insoluble double ferrocyanid, from which only traces of hydrocyanic acid are evolved by distillation with dilute mineral acid. For the purpose of overcoming these difficulties, Feld worked out a process which consisted in adding mercuric chlorid to the ferrocyanid whereby, under proper conditions, the whole of the cyanogen content of such ferrocyanid is converted into mercuric cyanid, from which the cyanogen may be recovered as hydrocyanic acid by distilling it with a suitable acid. Subsequently it was discovered by Dewrance and Williams (see British Patent No. 28,074/08) that a small proportion of cuprous or cupric salt in conjunction with a suitable acid effected the same result.

The present process constitutes in a sense an improvement on the aforesaid method of Dewrance and Williams being based on the discovery that in place of a copper salt (either cuprous or cupric), finely divided metallic copper may be employed, with a number of advantageous results, as will be presently pointed out. A further object of the process, viz., the speeding up of the reaction, where acids other than hydrochloric acid are used to bring about the conversion of ferrocyanids to hydrocyanic acid and cyanids, is accomplished by the addition of a small amount of ammonium chlorid or other chlorid. A further object is the maintenance of the concentration of the converting acid within proper limits, such limits being relatively narrow.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the annexed drawing and the following description setting forth in detail certain means and one mode of carrying out the invention, such disclosed means and mode illustrating, however, but one of various ways in which the principle of the invention may be used.

In said annexed drawing:—

The single figure there appearing is a diagrammatic representation of an apparatus designed for carrying out my present improved process.

Where employed in conjunction with a coke by-products recovery plant, material utilized in the present process will ordinarily be a sludge, such as obtained in the so-called Bueb process (see U. S. Patent No. 625,964, dated May 30, 1899) by treating the oven gases before removing the ammonia therefrom with a solution of iron sulfate, or copperas. It will be understood, however, that the present improvements are not limited to use with this particular material, but may be advantageously used with ferrocyanid compounds derived from various sources.

Referring to the aforesaid drawing, the familiar part of the apparatus, such as will be employed in the production of Bueb sludge, comprises a gas scrubber 1 in which the gas containing cyanogen compounds and ammonia is treated with a solution of a ferrous salt such as ferrous sulfate. A pump 2 serves to circulate the absorbing liquid through such scrubber, or to transfer the same in whole or part, when absorption has proceeded sufficiently, to a neutralizing tank 3. Here the solution is neutralized with an acid, such as sulfuric acid, to precipitate the soluble ferrocyanid, after which the mixture is elevated by means of a pump 4 to a filter press 5 or equivalent apparatus adapted to separate out such precipitate. The filtrate,

which is a solution of ammonium sulfate where ferrous sulfate has been used to extract the cyanids in the first step, is run into a tank 6, and such ammonium sulfate subsequently recovered by evaporation.

The filter cake from press 5, which will in the case in hand consist essentially of a double ferrocyanid of iron and ammonia, is transferred to an agitating tank 7 and mixed with water until it forms a thick mud. This mud or sludge is then run into a storage tank 8, from which it is fed as required into a suitable distilling vessel 10, the latter marking the beginning of the apparatus of special interest in connection with the process in hand.

This special apparatus comprises, in association with said still 10, a tank 11 containing sulfuric acid and connected to supply the latter to said still as desired; a combined condenser and fractioning column 12 where the steam evolved with the acid from said still is condensed and any hydrocyanic acid absorbed by the condensed steam is again distilled off before the condensed steam is discharged from the apparatus; and an absorber 13 connected with the upper part of said condenser, a fan 14 connected with said absorber serving to keep the latter, together with the condenser and still, under a slight vacuum, and thus prevent escape of hydrocyanic acid in case of any leak developing.

The lower end of the fractioning column 12 is connected by a trapped discharge pipe 15, so that the water condensing and collecting in said column may be discharged. Provision is also made for injecting steam into the base of said column as by a valve-control pipe 15^a in order to drive up into the upper condenser part thereof such hydrocyanic acid as is carried by such water as it passes down the column. The water discharged from the latter will accordingly be practically free of the acid.

The base of the still is connected with a discharge pipe 16, by means of which its contents, when the proper stage is reached, may be run into a settling tank or preferably through suitable filters 17 as shown, whereby the insoluble copper cyanid formed, as will presently be more fully explained, is separated out. The residual solution, consisting of ferrous sulfate, ammonium sulfate, free sulfuric acid and a slight amount of copper salts, is then run through a tank 18 filled with scrap iron on which the copper is deposited as the metal. The solution overflowing from tank 18 is collected in a tank 19 and then transferred by pump 20 back to scrubber 1, to be used over again.

The general operation of the apparatus just described in exemplification of my improved process may now be set forth as follows, viz.:—The distilling vessel 10 is charged with sulfuric (or hydrochloric) acid of the proper strength from tank 11. In case sulfuric acid is used, a small amount of ammonium chlorid, or other chlorid as heretofore indicated, is preferably added. A small quantity of metallic copper is then also added to said distilling vessel, such copper being preferably in a finely divided state, and thereupon the contents of the vessel are brought to boiling. When this stage is reached, the ferrocyanid compound is added gradually from tank 8, together with a further measured quantity of acid, to bring about the liberation of the hydrocyanic acid. In other words, the amount of free acid originally charged into the distilling vessel is maintained substantially constant by thus adding more acid along with the ferrocyanid compound, and by regulating the amount of heat applied and the quantity of water vapor driven off, the concentration of such acid in the distilling vessel will likewise remain substantially constant.

The manner in which the hydrocyanic acid that is freed by the reaction in the still is collected and separated, has been sufficiently indicated in connection with the description of the apparatus. The solution in the still will of course become gradually more and more concentrated with iron sulfate or chlorid, depending on which acid is used, and will have to be removed from such vessel after a time. As this condition is approached, no more acid is added with the ferrocyanid compound, the addition of the latter, however, being continued as fast as it is decomposed and hydrocyanic acid given off. In this way most of the acid originally charged into the distilling vessel is utilized, so that the final solution in such vessel contains very little free acid. No attempt is made to distil off the hydrocyanic acid completely as after the ferrocyanid compound has been decomposed with the formation of cuprous cyanid the evolution of hydrocyanic acid becomes extremely slow unless a further supply of ferrocyanid compound is added. The reaction is carried only so far until no ferrocyanid compounds remain undecomposed at which time considerable cyanogen will still remain combined as cuprous cyanid. Under these conditions the insoluble material remaining in the still which is essentially cuprous cyanid is easily separated from the solution by settling or filtration whereas if any undecomposed ferrocyanid compounds remain, the material settles very slowly and is difficult to filter.

Instead of recovering the copper in solution in the tank 18 by introducing metallic iron, it may be recovered electrolytically, as need not be described in detail. This metal-

lic copper, as well as the copper cyanid from the filters 17, is returned to the still for subsequent operation of the latter. If the ferrocyanid material used contains impurities such as tar or sulfur these impurities will gradually accumulate in the copper cyanid residue rendering the copper cyanid less active after repeated use. When this happens the copper cyanid residue is dried and incinerated whereby the impurities are burnt off and the residue of metallic copper is again used in the distilling vessels.

It will thus be seen that the copper may be used over and over again with a minimum of trouble, whereas if cuprous chlorid, for example, is used, the cuprous salt in the residual liquor has to be recovered by the addition of a soluble thiocyanate, thus precipitating cuprous thiocyanate which is not available for re-use directly. The employment of metallic copper in place of a copper salt also helps to counteract the action of atmospheric oxygen or ferric compounds in oxidizing cuprous to cupric compounds. The reaction is thus accelerated, since such cuprous compounds are much more active than the cupric compounds. Due to the manner in which the distillation is conducted by adding, along with the ferrocyanid compound, the proper quantity of acid for conversion of same, the concentration of the acid may be readily maintained within the proper narrow limits, *i. e.* high enough so that the reaction will proceed at a good speed, and yet not so high as to cause partial decomposition of the hydrocyanic acid evolved. At the same time I am able to avoid excessively diluting the alkali in which the hydrocyanic acid is absorbed. Finally it will be noted that by adding the ferrocyanid compound gradually, only a small amount of such compound remains undecomposed at any time, thus avoiding the effect of long continued boiling, which renders such compound more and more difficult to decompose into hydrocyanic acid.

Finally, the arrangement of the still, condenser and fractioning column permits the condensed water to flow through the fractioning column, be freed from hydrocyanic acid and then discharged from the apparatus instead of returning to the still. In this way, the capacity of the still is increased and a more concentrated solution of ferrous sulfate and ammonium sulfate obtained.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. The method of converting ferrocyanids to hydrocyanic acid and cyanids, which consists in treating the ferrocyanid with metallic copper in conjunction with an acid capable of reacting with such ferrocyanid and distilling off the hydrocyanic acid thereupon set free.

2. The method of converting ferrocyanids to hydrocyanic acid and cyanids, which consists in treating the ferrocyanid with finely divided metallic copper in conjunction with an acid capable of reacting with such ferrocyanid and distilling off the hydrocyanic acid thereupon set free.

3. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing metallic copper with an acid capable of reacting with such ferrocyanid, gradually adding the ferrocyanid along with a further quantity of such acid, and distilling off the hydrocyanic acid thereupon set free.

4. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing metallic copper with an acid capable of reacting with such ferrocyanid, gradually adding the ferrocyanid along with a further quantity of such acid approximately sufficient to react with such ferrocyanid, whereby the amount of free acid present is maintained substantially constant, and distilling off the hydrocyanic acid thereupon set free.

5. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing finely divided metallic copper with a quantity of sulfuric acid admixed with a small amount of ammonium chlorid, gradually adding the ferrocyanid along with a further quantity of such acid, and distilling off the hydrocyanic acid thereupon set free.

6. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing finely divided metallic copper with a quantity of sulfuric acid admixed with a small amount of ammonium chlorid, gradually adding the ferrocyanid along with a further quantity of such acid approximately sufficient to react with such ferrocyanid, whereby the amount of free acid present is maintained substantially constant, and distilling off the hydrocyanic acid thereupon set free.

7. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing metallic copper with an acid capable of reacting with such ferrocyanid, gradually adding the ferrocyanid along with a further quantity of such acid approximately sufficient to react with such ferrocyanid, whereby the amount of reacting acid present is maintained substantially constant, and distilling off the hydrocyanic acid set free, the addition of

such further quantity of reacting acid being discontinued when the solution becomes concentrated with the iron salt of such acid.

8. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing metallic copper with an acid capable of reacting with such ferrocyanid, gradually adding the ferrocyanid along with a further quantity of such acid, distilling off the hydrocyanic acid thereupon set free, and subsequently recovering the copper from the solution.

9. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing metallic copper with an acid capable of reacting with such ferrocyanid, gradually adding the ferrocyanid along with a further quantity of such acid, distilling off the hydrocyanic acid thereupon set free, separating out the insoluble copper cyanid in such solution, and then recovering the copper in metallic form from the copper compounds remaining in such solution.

10. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing metallic copper with an acid capable of reacting with such ferrocyanid, gradually adding the ferrocyanid along with a further quantity of such acid, distilling off the hydrocyanic acid thereupon set free, and subsequently recovering the copper from the solution, and utilizing the same over again in such distilling step.

11. In a method of converting ferrocyanids to hydrocyanic acid and cyanids, the steps which consist in placing metallic copper with a suitable acid, gradually adding the ferrocyanid along with a further quantity of such acid, distilling off the hydrocyanic acid thereupon set free, separating out the insoluble copper cyanid in such solution, and then recovering the copper in metallic form from the copper compounds remaining in such solution and utilizing both such copper cyanid and metallic copper over again in such distilling step.

Signed by me this 20th day of August, 1919.

MAX E. MUELLER.